

2015-1075

**IN THE
UNITED STATES COURT OF APPEALS
FOR THE FEDERAL CIRCUIT**

NESTE OIL OYJ,
Appellant,

v.

REG SYNTHETIC FUELS, LLC,
Appellee.

**Appeal from the United States Patent and Trademark Office,
Patent Trial and Appeal Board, in Case IPR2013-00178.**

BRIEF FOR APPELLANT-PATENT OWNER NESTE OIL OYJ

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CERTIFICATE OF INTEREST

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1. The full name of every party or amicus represented by me is:

Neste Oil Oyj.
2. The name of the real party in interest (if the party named in the caption is not the real party in interest) represented by me is:

None.
3. All parent corporations and any publicly held companies that own 10 percent or more of the stock of the party or amicus curiae represented by me are:

None.
4. The names of all law firms and the partners or associates that appeared for the party or amicus now represented by me in the trial court or agency or are expected to appear in this court are:

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STATEMENT OF RELATED CASES

No appeal in or from the same proceeding in the lower court or body was previously before this or any other appellate court.

JURISDICTIONAL STATEMENT

The U.S. Patent and Trademark Office's Patent Trial and Appeal Board ("Board") had jurisdiction over this *inter partes* review proceeding under 35 U.S.C. § 6. The Board entered its final written decision pursuant to 35 U.S.C. § 318(a) and 37 C.F.R. § 42.73 on August 29, 2014. Neste Oil Oyj filed a timely notice of appeal on September 18, 2014. This Court has jurisdiction under 28 U.S.C. § 1295(a)(4)(A) and 35 U.S.C. § 141(c).

STATEMENT OF THE ISSUES

1. Whether the Board erred as a matter of law in concluding that proposed claim 22 would have been obvious when the Board focused only on two individual claim limitations and failed to analyze claim 22 as a whole, including the claim's requirement for a biological feedstock having more than 5 wt.% free fatty acids; and that error was harmful in light of Neste's unchallenged evidence that hydrodeoxygenation (HDO) reaction temperatures were known to be dependent on feedstock type and therefore one of ordinary skill would not have selected HDO reaction temperatures within the claimed range (280-330 °C) with feedstocks containing more than 5 wt.% free fatty acids.

2. Whether the Board erred in holding that the prior art did not teach away from HDO reaction temperatures within the claimed range when it misapplied the overlapping ranges principle of *In re Peterson*, 315 F.3d 1325 (Fed. Cir. 2003); disregarded unchallenged evidence that the Craig reference concluded from a detailed temperature study that HDO of biological feedstocks at temperatures below 350 °C did not work due to reactor plugging; misinterpreted the Jakkula reference's published results; and failed to analyze the Monnier reference and other prior art that supported nonobviousness.

STATEMENT OF THE CASE

In March 2013, Syntroleum Corporation petitioned for *inter partes* review (IPR) of claims 1-20 of U.S. Patent No. 8,212,094, owned by Neste. After Neste submitted a preliminary response, the Board instituted an IPR of claims 1-20 on September 4, 2013.

Neste elected not to file a patent owner response and instead moved to amend the '094 patent by substituting proposed claims 21-30 for the original claims. Neste's motion was supported by expert declarations from Dr. Michael T. Klein.

The Board held an oral hearing on April 1, 2014. On June 24, 2014, REG Synthetic Fuels, LLC filed updated mandatory notices informing the Board that it had acquired Syntroleum Corporation. On August 29, 2014, the Board issued its

final written decision granting Neste's motion to amend only as to cancelation of claims 1-20. The Board held that proposed claims 21 and 24-30 lacked written description support and that claims 21-30 were obvious in view of the prior art. This appeal followed.

I. PRELIMINARY STATEMENT

This appeal arises from the Board's final written decision in an IPR of the '094 patent. To narrow the issues on appeal, Neste will focus on the patentability of claim 22, which was *not* held unpatentable on written description grounds. Thus, this Court need not address any written description issue in this appeal. The only issue is whether the Board erred as a matter of law in concluding that the subject matter of proposed claim 22 would have been obvious.

Claim 22 defines a process for converting biological feedstocks containing more than 5 wt.% free fatty acids into diesel-range n-paraffins with minimal formation of undesired high molecular weight hydrocarbons (less than 1 wt.%). The claimed process uses a reduced HDO reaction temperature (280-330 °C) compared to the prior art; low levels of contaminants in the total feed (less than 1 w-ppm alkali and alkaline earth metals, less than 1 w-ppm other metals, and less than 5 w-ppm phosphorous); and a 5-30:1 ratio of diluting agent to fresh feed in the total feed. This specific *combination* of features defines the claimed process.

The Board, however, only considered whether two *individual* claim limitations rendered claim 22 patentable without analyzing or making any findings regarding the combined features of claim 22 or the obviousness or nonobviousness of claim 22 as a whole. This was harmful legal error. Claim 22, for example, specifically requires a biological feedstock containing more than 5 wt.% free fatty acids, and Neste presented unchallenged evidence that the prior art taught that HDO reaction temperature depended on the particular type of feedstock and that higher HDO temperatures were believed to be needed for feedstocks containing free fatty acids. Yet the Board never addressed the claim requirement for more than 5 wt.% free fatty acids or the prior art's teaching of the dependence of HDO temperature on feedstock type. The Board's obviousness analysis was therefore flawed as a matter of law.

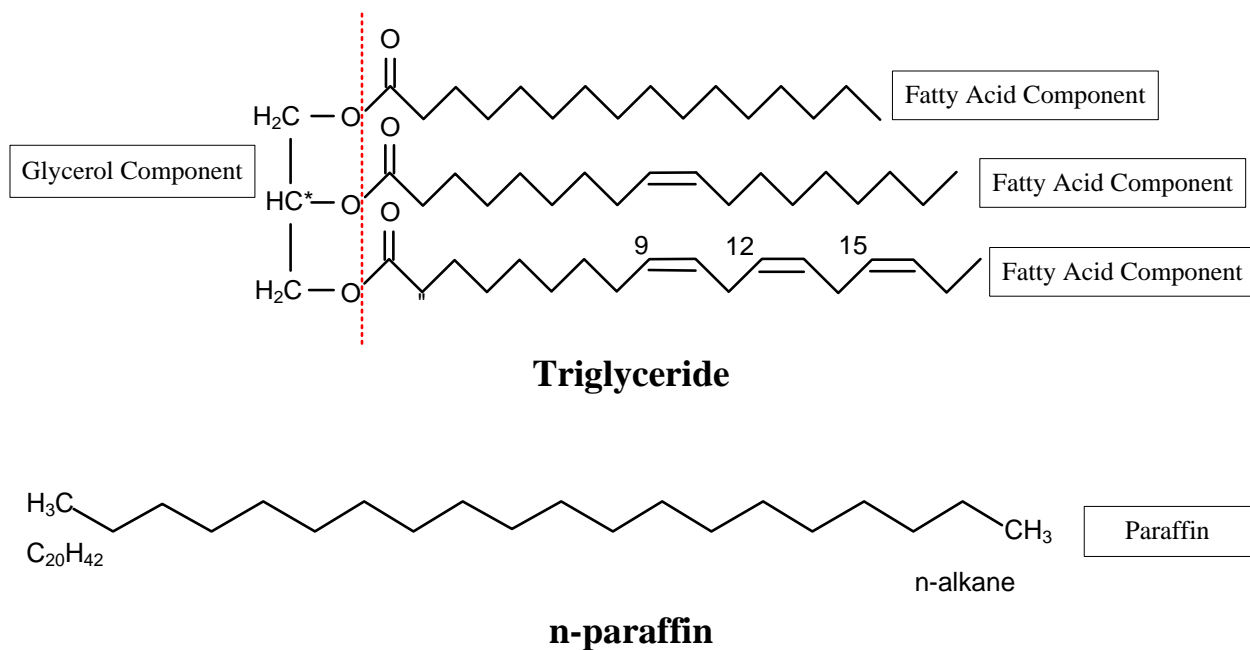
In addition, the Board misapplied the "overlapping ranges" principle of *In re Peterson*, 315 F.3d 1325 (Fed. Cir. 2003), and incorrectly concluded that the prior art did not teach away from HDO reaction temperatures in the claimed range. Considered as a whole and without hindsight, the specific combination of features of claim 22 would not have been obvious to one of ordinary skill in the art as of the July 2005 priority date. The Board's legally erroneous conclusion to the contrary should be reversed.

II. STATEMENT OF FACTS

Neste's motion to amend was supported by expert declarations from Dr. Michael T. Klein. (A2141-2188; A2189-2244; A3259-3286.) Dr. Klein, the Dan Rich Chair of Energy at the University of Delaware, directs the Delaware Energy Institute. (A2145 at ¶ 5; A3333.) He received his Sc.D. in Chemical Engineering from MIT and has over 30 years of experience. (A2145 at ¶ 6; A2193 at ¶ 4; A3333-3343.) His areas of expertise include upgrading and converting renewable and fossil fuels; chemical reaction engineering; and detailed kinetic modeling of complex reaction systems. (A2193 at ¶ 4; A2359-3286; A2145-2146 at ¶¶ 6-7.) Dr. Klein is the Editor-in-Chief of the American Chemical Society journal *Energy and Fuels*, which is dedicated in part to fuels such as diesel-range hydrocarbons. (A2194 at ¶ 5; A2145 at ¶ 6.) He has directed graduate and undergraduate students performing research into the HDO of model compounds that mimic functional groups in biological feedstocks. (A2193 at ¶ 5.) This work includes overseeing the operation of HDO reactors. (A2193-2194 at ¶ 5.) Dr. Klein has received a number of awards for his work, including the R.H. Wilhelm Award in Chemical Reaction Engineering. (A2193 at ¶ 4; A3333-3334.) The facts summarized below are supported by Dr. Klein's testimony and other cited evidence.

A. Hydrotreating Technology

For environmental reasons and to meet increasing demand, fuel producers have sought to use renewable biological materials such as vegetable oils, wood oils, and animal fats to manufacture diesel fuels. (A59 at 1:25-30; A62 at 7:49-65.) Naturally occurring biological oils and fats consist mainly of triglycerides (three fatty acid chains bonded to a glycerol moiety). (A62 at 7:21-40.) During hydrotreating, the triglycerides and fatty acids present in oils and fats are reacted with hydrogen in the presence of a hydrotreating catalyst to form n-paraffins (saturated hydrocarbons). (A2148-2149 at ¶¶ 12-13.)



(A2149.)

Converting natural triglycerides and fatty acids into paraffin compositions involves saturating double bonds (by adding hydrogen) and removing oxygenates

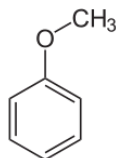
(-OH, -COH, -COOH, etc.). (A2149 at ¶ 13.) Hydrodeoxygenation, or HDO, removes oxygen in the form of water and replaces it with hydrogen. (A60 at 4:62-65; A2149 at ¶ 13.) The resulting n-paraffin composition can be used directly as a diesel fuel or diesel fuel additive. (A60 at 4:23-40; A63 at 10:57-61.)

Selecting reactor operating temperature for the HDO reaction is a different issue from using dilution to control the reaction heat generated during HDO. (A2152 at ¶ 20; A2173 at ¶ 59.) HDO is an exothermic reaction that, in the absence of heat transfer, will cause the initial reactor operating temperature to rise in the reactor as the reaction progresses. (A2152 at ¶ 20; A2173 at ¶ 59.) A diluting agent may be used to reduce the reaction temperature rise over the course of the reactor, but does not change the initial reactor operating temperature. (A2152 at ¶ 20; A2173 at ¶ 59.)

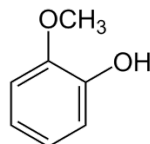
B. Biological Feedstocks

Feed streams of biological origin are composed of complex mixtures of triglycerides and free fatty acids, with a wide range of carbon numbers and degrees of unsaturation. (A2194-2196 at ¶¶ 7-12; A59 at 2:14-16, 2:24-31; A62 at 7:59-65; A3333-3343; A3350 at Table 8.2, Table 8.3; *see also* A2707 at ¶ 65.) In contrast, some literature in this field details experiments performed on so-called “model” compounds, such as anisole and guaiacol. These are single components or simple two- or three-component mixtures with low carbon numbers and different chemical

structures, functional groups, and carbon numbers from feed streams of biological origin. (A2221-2228 at ¶¶ 46-58; A62 at 7:49-65; A2674-2675 at ¶ 11.)



Anisole



Guaiacol

(A2224.)

While most fatty acids found in biological feedstocks are in the triglyceride form, certain biological feedstocks contain “free” fatty acids. (A2194 at ¶ 7; A59 at 2:9-12, 2:24-36; A2331 at Table 3.160.) Free fatty acids are composed of fatty acid chains not attached to other molecules (i.e., a carboxylic acid with a hydrocarbon chain). (A2153-2154 at ¶ 22.) Vegetable oils typically contain lower amounts of free fatty acids than wood oils or animal fats. (A2194 at ¶ 7; A59 at 2:29-31.) “Tall oil” is a by-product of the pulping of pine wood. (A2311.) Crude tall oil is a mixture of free fatty acids, resin, and unsaponifiables, with “tall oil fatty acid” being the fatty acid fraction of crude tall oil. (A2194-2195 at ¶ 7; A2311-2312.)

The free fatty acid contents of several oils and fats are listed below:

Oil Type	Free Fatty Acid Content
Canola oil	0.4-1% (A2475; <i>see</i> A2634 at 155:2-12.)
Rapeseed oil	0.1 wt.% (A2659 at Table V.) 0.1-1% for crude (A2300.) 0.05% for alkali refined (A2300.)
Sunflower oil	0.1 wt.% (A2659 at Table V.)

Oil Type	Free Fatty Acid Content
Soybean oil	Good-quality oil has FFA content of 0.5% (A2306; A2659 at Table V.)
Corn oil	Crude normally contains less than 3% (A2272.)
Coconut oil	Higher quality oils have free fatty acid content of 3% (A2269.) Crude often exceeds 5% (A2269.)
Palm oil	Quality palm oils: 2-3% (A2292); 0.1 wt.% (A2659 at Table V.)
Tall oil fatty acid	90-98 wt.% (A2312.)
Depitched tall oil	52 wt.% (A2665 at 4:5-9.)
Finnish tall oil	45 wt.% (A2666 at 6:1-2.)
Aspen wood oils	60 wt.% (A2666 at 5:35-40.) 58 wt.% (A2666 at 5:35-40.)
Restaurant yellow grease	American Fats and Oils Association standard for yellow grease is 15% free fatty acids. (A2370; <i>see</i> A2675 at ¶ 13.)
Animal tallow	American Fats and Oils Association standard for tallow ranges from 2-35% free fatty acids depending on the type of tallow. (A2370; A2675 at ¶ 13.)
Waste restaurant oil	May contain yellow and/or brown grease. (A2733 at [0004]; A2667 at 8:3-7.) American Fats and Oils Association standard for yellow grease is 15% free fatty acids. (A2370; <i>see</i> A2675 at ¶ 13.)

(A2195-2196.)

C. The Invention of the '094 Patent

The '094 patent addresses the competing chemical reactions that occur when biological oils and fats undergo HDO. (A2153 at ¶ 22.) The desired reactions convert triglycerides and free fatty acids to n-paraffins. (A2153-2154 at ¶ 22.) Undesired reactions also occur, however, including the formation of high molecular weight hydrocarbons. (A2154 at ¶ 22; A59 at 2:19-23.) High molecular

weight hydrocarbons reduce the HDO reaction's selectivity for n-paraffins and decrease diesel yield. (A2154 at ¶ 22; A65 at 13:34-14:3.)

Through a series of experiments described in the '094 patent, the inventors determined that the presence of more than 5 wt.% free fatty acids, and particular levels of metals and phosphorous, in a fresh biological feedstock promote the formation of high molecular weight hydrocarbons during HDO. (A2154-2155 at ¶ 23; A59 at 2:9-12; A63 at 9:62-66; A65 at 14:29-34; A64-66 at Examples 1-7.) They found that reaction selectivity could be controlled by manipulating the reaction temperature, concentration of reactant, and contaminant levels. (A2154-2155 at ¶ 23.) Specifically, they combined a reduced HDO reaction temperature of 280-330 °C with a 5-30:1 ratio of diluting agent to fresh feed in the "total" feed (biological feedstock plus diluting agent) and particular maximum levels of specified contaminants in the total feed: less than 1 w-ppm alkali and alkaline earth metals; less than 1 w-ppm other metals; and less than 5 w-ppm phosphorous. (A2155 at ¶ 24.) This unique combination of process parameters resulted in nearly complete HDO conversion with high selectivity for forming n-paraffins while minimizing the formation of high molecular weight hydrocarbons. (A2155 at ¶ 24; A63 at 9:55-10:7; A64 at 11:3-23; A65 at 14:28-34; A61 at 6:8-58.)

The Board only briefly addressed one of the examples (Example 5) of the '094 patent. (A44-45.) A more complete summary of the experimental work disclosed in the specification is provided below. (A2156-2161 at ¶¶ 25-34.)

Examples 1 and 2 show that HDO reaction temperatures of 340-360 °C are not low enough to prevent high molecular weight hydrocarbons from forming when the fresh biological feedstock contains higher amounts of free fatty acids. (A2157-2158 at ¶ 26.) Hydrodeoxygenating a fresh feed containing 100% free fatty acids (no dilution) produced about 7 wt.% high molecular weight hydrocarbons both at 340-360 °C and at a higher temperature, 370-385 °C. (A2157-2158 at ¶ 26; A64 at 11:30-12:25, Table 1; A58 at Figure 8.)

Data from Examples 4 and 5 also show that temperature alone is not enough to prevent high molecular weight hydrocarbons from forming. (A2158 at ¶ 27.) In Example 5, hydrodeoxygenating a fresh feedstock containing 10.7 wt.% free fatty acids, without dilution, formed 5.7 wt.% high molecular weight hydrocarbons at an HDO temperature of 305 °C. (A2158 at ¶ 27; A65 at Table 3.) In Example 4, hydrodeoxygenating a fresh feedstock containing 10.7 wt.% free fatty acids, without dilution, increased the formation of high molecular weight hydrocarbons from about 3 wt.% to about 8 wt.% at 305 °C. (A2158 at ¶ 27; A65 at 13:20-14:7; A55 at Figure 2.) As such, reduced HDO reaction temperature alone did not

prevent high molecular weight hydrocarbons from forming when the fresh feedstock contained more than 5 wt.% free fatty acids. (A2158 at ¶ 27.)

Example 3 demonstrates the importance of low contaminant levels. (A2158-2159 at ¶ 28.) It shows that complete HDO conversion of crude feedstocks without dilution requires higher reaction temperatures. (A2158-2159 at ¶ 28.) Crude rapeseed oil contained 90 ppm total metals and 110 ppm phosphorous, while purified rapeseed oil contained less than 1 ppm phosphorous. (A2158 at ¶ 28.) Both feedstocks contained less than 1% free fatty acids. (A2158-2159 at ¶ 28; A64 at Table 2.) Without dilution, the pure rapeseed oil achieved complete HDO conversion at a lower temperature (305 °C) than the crude rapeseed oil (330 °C). (A2159 at ¶ 28; A64 at 12:30-13:7, Table 2; A56 at Figure 4.)

Example 3 also illustrates that higher levels of free fatty acids, metals, and phosphorous in the fresh feedstock cause more high molecular weight hydrocarbons to form compared to purified feedstocks, even with low temperatures and product recycle (dilution). (A2159 at ¶ 29.) Purified rapeseed oil and crude animal fat were hydrodeoxygenated at a reduced HDO temperature (305 °C) with a 5:1 dilution ratio (reported as the reciprocal 1:5 ratio of fresh feed to diluting agent). (A2159 at ¶ 29.) The purified rapeseed oil (containing 0.7 wt.% free fatty acids and less than 1 ppm phosphorous) produced less than 1 wt.% high molecular weight hydrocarbons. (A2159 at ¶ 29.) In contrast, the crude animal fat (containing

10.8 wt.% free fatty acids, 163 ppm metals, and 86 ppm phosphorous) produced more than 1 wt.% high molecular weight hydrocarbons and did not achieve complete HDO conversion. (A2159 at ¶ 29; A65 at 13:8-13:19; A64 at Table 2; A56 at Figure 5.)

Example 4 shows that higher levels of free fatty acids in the fresh feedstock without dilution increase the formation of high molecular weight hydrocarbons. (A2159 at ¶ 30.) Purified rapeseed oil (containing 0.7 wt.% free fatty acids) produced about 3 wt.% high molecular weight hydrocarbons. (A2159 at ¶ 30.) When this feed was spiked with 10 wt.% free fatty acids, the amount of high molecular weight hydrocarbons formed increased to about 8 wt.%. (A2159 at ¶ 30; A65 at 13:35-37; A64 at Table 2; A55 at Figure 2.)

Example 5 demonstrates the benefits of dilution combined with reduced HDO temperature in preventing high molecular weight hydrocarbons from forming when the fresh feedstock contains more than 5 wt.% free fatty acids. (A2160 at ¶ 31.) Hydrodeoxygenating a fresh feedstock containing 10.7 wt.% free fatty acids at 305 °C, without dilution, increased the formation of high molecular weight hydrocarbons to 5.7 wt.%. (A2160 at ¶ 31.) Accordingly, low temperature and low contaminants in the feed were not enough to prevent high molecular weight hydrocarbons from forming. (A2160 at ¶ 31.) Significantly, however, adding a 5:1 dilution (containing about 0.4 wt.% high molecular weight hydrocarbons) to this

process resulted in only 0.4 wt.% high molecular weight hydrocarbons in the hydrodeoxygenated product. (A2160 at ¶ 31; A65 at 14:10-37; A64 at Table 2; A55 at Figure 3.)

Example 6 illustrates that reducing HDO reaction temperature to 280-330 °C results in almost theoretical n-paraffin yield without significant side reactions compared to higher HDO temperatures of 340-360 °C, which resulted in a high amount of side reactions and low n-paraffin yield. (A2160 at ¶ 32; A66 at 15:5-54; A57 at Figure 6.)

Example 7 reports that less than 1 wt.% high molecular weight hydrocarbons were formed during HDO of palm oil containing 1.2 wt.% free fatty acids and other contaminants at a reaction temperature of 300-305 °C and 5:1 recycle (dilution) ratio of diluting agent to fresh feed (again reported as the reciprocal 1:5 ratio of fresh feed to diluting agent). (A2160-2161 at ¶ 33.) The level of high molecular weight hydrocarbons remained this low for nine months. (A2161 at ¶ 33; A66 at 15:60-16:9, Table 4; A57 at Figure 7.)

In summary, through this series of experiments the inventors determined that, within this reaction network, when the fresh biological feedstock contains more than 5 wt.% free fatty acids and particular levels of metallic and phosphorous contaminants, undesirable high molecular weight hydrocarbons were formed. (A2161 at ¶ 34.) By combining a reduced HDO reaction temperature of

280-330 °C, low levels of contaminants (metals and phosphorus), and a 5-30:1 ratio of diluting agent to fresh feed in the total feed, a hydrodeoxygenated product containing less than 1 wt.% of high molecular weight hydrocarbons was achieved. (A2161 at ¶ 34.)

D. The Prior Art

1. Craig

U.S. Patent No. 4,992,605 to Craig et al. describes a process for producing liquid paraffinic diesel-range hydrocarbons by hydroprocessing vegetable oils using a commercially available hydroprocessing catalyst. (A2170-2171 at ¶ 53; A2856 at abstract; A2857 at 2:40-65; A2862 at 11:45-50; A2861 at 10:20-23.) The water yields and types of n-paraffins obtained indicate an HDO process. (A2171 at ¶ 53; *see* A2857 at 2:44-50; A2858 at 3:29-4:10; A2859 at Table 3 and Table 4; A2861 at Table 9.) REG's technical expert, Dr. Edward L. Sughrue, described the Craig reference as "the gold standard" in the art. (A2908-2910 at 46:20-48:3.)

Craig performed a series of experiments to determine optimum conditions, including temperatures, for HDO of vegetable oils. (A2171 at ¶ 54; A2859 at 6:48-53; A2860 at 7:11-14.) Craig concluded that "350° C. was the *lower limit* for trouble free operation" and that "[a]t temperatures of 350° C. and lower, the product collection system *was plugged* with a solid margarine-like material." (A2860 at 7:11-14 (emphasis added); A2861 at 10:17-19 (emphasis added); A2171

at ¶ 54.) Craig also determined that at temperatures up to 320 °C non-suitable solid or semi-solid materials were formed. (A2171 at ¶ 54; A2862 at 11:13-16.) Notably, the only experiment without results in Craig's Table 1 was at a temperature of 320 °C. (A2171 at ¶ 54; A2858 at Table 1.) Thus, Craig's disclosure that 350 °C was the lower limit for hydroprocessing would have discouraged one of ordinary skill from choosing lower HDO reaction temperatures, which Craig warned do not work. (A2134; A2172 at ¶ 56; A2860 at 7:11-13; A2862 at 11:13-16; A2861 at 10:17-19, Table 8; A2941-2942 at 79:16-80:20.) Dr. Sughrue never addressed Craig's teaching of reactor plugging at temperatures below 350 °C. (*See, e.g.*, A2686 at ¶ 31; A2687 at ¶ 33; A2689 at ¶¶ 36, 37; A2693 at ¶ 42; A2705 at ¶ 60; A2722-2723 at ¶ 90.) He never used the word "plug" or "plugging" in either of his declarations responding to Neste's motion to amend. (*See, e.g., id.*)

Craig's Table 8 lists the ranges of HDO temperatures for various oils and their optimum processing temperatures. (A2171 at ¶ 55; A2861 at Table 8.) The HDO temperatures range from 350-450 °C with optimum temperatures from 360-390 °C. (A2171 at ¶ 55; A2861 at Table 8.) Craig states that higher temperatures had minimal effect on yields and that the liquid product was almost completely converted to high quality diesel-range material. (A2171-2172 at ¶ 55; A2860 at 7:13-14; A2862 at 11:35-40.)

One of ordinary skill would have understood from Craig that HDO reaction temperature is feedstock dependent. (A2210 at ¶ 30.) Craig, for example, specifically states that HDO reaction temperature is “dependent on the feedstock.” (A2210 at ¶ 30; A2857-2858 at 2:66-3:1.) Dr. Sughrue did not dispute this. (*See, e.g.*, A2686 at ¶ 31; A2687 at ¶ 33; A2689 at ¶¶ 36, 37; A2693 at ¶ 42; A2705 at ¶ 60; A2722-2723 at ¶ 90.) For tall oil fatty acid (TOFA), which contains more than 5 wt.% free fatty acids, Craig describes an HDO temperature of 380-450 °C with an optimum temperature of 390 °C. (A2210-2211 at ¶ 30; A2861 at Table 8; A2862 at 12:30-34.) Consistent with this 390 °C optimum temperature, Craig states that tall oil fatty acid “was processed at somewhat higher temperatures than that utilized for the vegetable oils.” (A2861 at 9:38-10:19; A2210 at ¶ 29.)

Though Craig used a bench-scale reactor, REG’s expert Dr. Sughrue testified that he did not believe this reactor configuration “would cause any difference in [Craig’s] conclusions or in [Craig’s] results” and that he knew of nothing to discredit Craig’s work. (A2908-2910 at 46:20-48:3; A2940 at 78:5-10; A2941 at 79:2-15; A2219-2220 at ¶ 43.)

2. Monnier and Other Prior Art Not Addressed by the Board

Craig’s HDO reaction temperatures are consistent with those of U.S. Patent No. 5,705,722 to Monnier et al., which also discloses HDO of biomass feedstocks containing more than 5 wt.% free fatty acids. (A2173-2174 at ¶ 60; A2664 at

1:56-67.) The Board's decision did not address Monnier. Monnier produced biomass feedstock from tall oil containing 30-60 wt.% fatty acids, wood oils, animal fats, and blends of tall oil with plants and vegetable oils containing substantial amounts of fatty acids or with animal fats. (A2211 at ¶ 31; A2664 at 1:58-67.) The fatty acids in Monnier's tall oil were free fatty acids. (A2211 at ¶ 31; A2311; A2809-2810 at 70:6:-71:1.) For these feedstocks, Monnier states that the reaction temperature should be at least 350 °C and preferably at least 370 °C, with the normal optimum operating temperature in the range of 370-450 °C. (A2211 at ¶ 31; A2664 at 2:56-58.)

Monnier's working examples used depitched tall oil, wood oil, restaurant yellow grease, animal tallow, yellow grease mixed with vegetable or plant oil, or a mixture of 75 volume percent depitched tall oil and 25 volume percent canola oil. (A2211-2212 at ¶ 31; A2665 at 4:5-15; A2666 at 5:33-43, 5:65-6:5, 6:30-55; A2667 at 7:20-45, 8:2-10, 8:34-42.) The approximate or reported free fatty acid content of these feedstocks and Monnier's corresponding HDO reaction temperatures are listed below.

Oil Type	Free Fatty Acid Content	Monnier's HDO Reaction Temperature
Depitched tall oil	52 wt.% (A2665 at 4:5-9.)	410 °C (A2665 at 4:5-15.)
Finnish tall oil	45 wt.% (A2666 at 6:1-2.)	400 °C (A2666 at 5:65-6:5.)

Oil Type	Free Fatty Acid Content	Monnier's HDO Reaction Temperature
Aspen wood oils	60 wt.% (A2666 at 5:35-40.) 58 wt.% (A2666 at 5:35-40.)	380 °C (A2666 at 5:33-43.)
Restaurant yellow grease	American Fats and Oils Association standard for yellow grease is 15% free fatty acids. (A2370; A2675 at ¶ 13.)	370 °C (A2666 at 6:30-55.)
Animal tallow	American Fats and Oils Association standard for tallow ranges from 2-35% free fatty acids depending on the type of tallow. (A2370; A2675 at ¶ 13.)	370 °C (A2667 at 7:19-45.)
Waste restaurant oil	May contain yellow and/or brown grease. (A2733 at [0004]; A2667 at 8:3-7.) American Fats and Oils Association standard for yellow grease is 15% free fatty acids. (A2370; A2675 at ¶ 13.)	370 °C (A2667 at 8:1-10.)
75 vol. % depitched tall oil and 25 vol. % canola oil	Assume 75 vol.% of 52 wt.% of free fatty acids found in depitched tall oil = approx. 39 wt.%. (A2212; A2665 at 4:5-9.)	400 °C (A2667 at 8:33-42.)

(A2212.)

Monnier therefore specifically addressed the HDO of biological feedstocks containing more than 5 wt.% free fatty acids. (A2212 at ¶ 32.) For these feedstocks, Monnier described reaction temperatures of at least 350 °C and working examples at 370-410 °C. (A2212-2213 at ¶ 32.)

W. Craig & E. Coxworth, “A Marketing Survey of Worldwide Potential for Use of Vegetable Oil Conversion Products in Diesel Fuel,” SRC Publication No. R-1520-2-C-89 (October 1989) (“Coxworth”), describes hydrodeoxygenating

crude tall oil and depitched tall oil, which both contain more than 5 wt.% free fatty acids, using NiMo and HDS-20 catalysts. (A2176 at ¶ 65; A2984; A3085; A3100.) Coxworth uses HDO reaction temperatures of 370 °C and 360 °C for these feedstocks, respectively, consistent with the high HDO reaction temperatures disclosed in Craig. (A2176 at ¶ 65; A3085; A3100.)

Swedish Patent 520633 (“SE ’633”) discloses the hydrogenation of the fatty acids or triglycerides of vegetable oils such as rapeseed oil and tall oil fatty acid to yield n-paraffins using commonly available catalysts. (A2175 at ¶ 63; A3199-3201.) Rapeseed oil contains less than 5 wt.% free fatty acids. (A2659 at Table V; A2300.) Tall oil fatty acid contains 90-98 wt.% free fatty acids. (A2312.) The hydrogenation temperature disclosed in SE ’633 is 330-450 °C with a recommended temperature of about 390 °C. (A2175 at ¶ 63; A3201.)

3. CZ ’575

Czech Republic Patent Number 283575 to Oldrich et al. (“CZ ’575”) discloses HDO of rapeseed oil at a temperature of 250-425 °C, more particularly from 320-375 °C. (A2175 at ¶ 64; A3174-3175.) A working example describes hydrotreating raw rapeseed oil at 350 °C. (A2175 at ¶ 64; A3176 at Table 2.) CZ ’575 does not report HDO of any feedstock having more than 5 wt.% free fatty acids. (A2215 at ¶ 35.) In addition, the goal of the process was to obtain a predominantly hydrocracked product, which has a different chemical structure

from the isomerized product produced by the claimed process. (A2176 at ¶ 64.) Finally, although CZ '575 discloses adding a petroleum fraction during hydrogenation, this is not a diluting agent containing hydrocarbons of biological origin as specified in proposed substitute claim 22. (A2176 at ¶ 64.)

4. Harrison

U.S. Patent No. 5,093,535 to Harrison et al. is a general reference not specific to any particular type of hydrogenation. (A2179 at ¶ 70; A3215.) Harrison describes a broad hydrogenation temperature range of 40-380 °C with no indication of what temperature would be appropriate for HDO or for what feedstocks. (A2179 at ¶ 70; A3226 at 1:5-23.) It also discloses a temperature range of 260-375 °C for hydrodesulfurization. (A2179 at ¶ 70; A3226 at 2:10-20.) No examples or specific HDO temperatures are disclosed for feedstocks having more than 5 wt.% free fatty acids. (A2215 at ¶ 35.)

5. Jakkula

European Patent Application Publication EP 1 396 531 A2 to Jakkula et al. discloses a process for producing a hydrocarbon component of biological origin, including an HDO step. (A2169 at ¶ 50; A3243.) Jakkula does not disclose forming a hydrodeoxygenated product containing less than 1 wt.% of high molecular weight hydrocarbons. (A2169 at ¶ 50.) In fact, Jakkula provides no compositional information for the product produced by its HDO process. (A2169 at ¶ 50; *see*

A3250.) It also does not disclose the contaminant levels of the total feed stream. (A2169 at ¶ 50.)

Jakkula provides only a general statement that the HDO “temperature varies between 200 and 500 °C, preferably in the range of 300-400 °C.” (A2170 at ¶ 51; A3245 at [0020].) No specific parameters or examples are provided for HDO reaction temperatures. (A2170 at ¶ 51.) Example 1 of Jakkula refers to HDO of tall oil fatty acid (TOFA), but does not disclose the HDO reaction temperature used. (A2170 at ¶ 51; A3250 at [0070].) That is the only HDO example in Jakkula. (A2170 at ¶ 51.) Therefore, Jakkula does not describe the specific HDO temperature range of 280-330 °C of claim 22. (A2170 at ¶ 51.)

Jakkula lists a wide range of potential biological feedstocks, including:

wood-based and other plant-based fats and oils such as rapeseed oil, colza oil, canola oil, tall oil, sunflower oil, soybean oil, hempseed oil, olive oil, linseed oil, mustard oil, palm oil, peanut oil, castor oil, coconut oil, as well as fats contained in plants bred by means of gene manipulation, animal-based fats such as lard, tallow, train oil, and fats contained in milk, as well as recycled fats of the food industry and mixtures of the above.

(A2214-2215 at ¶ 35; A3245 at [0017].) But Jakkula does not report any specific HDO reaction temperature for any individual feedstock, including for a feedstock such as tall oil fatty acid containing more than 5 wt.% free fatty acids. (A2215 at ¶ 35.)

One of ordinary skill faced with the general and broad range of HDO reaction temperatures of Jakkula would consult Craig for more specific guidance because, as shown below, Craig's detailed temperature study used a similar HDO process with similar feedstocks, pressures, and catalysts. (A2172-2173 at ¶ 57; *compare* A3245 at [0017], [0020], A3250 at [0070] *with* A2857 at 2:40-65, A2860-2861 at 7:8-10:19, Table 8.)

Operating Parameter	Jakkula	Craig
Catalyst	Known hydrogenation catalysts including CoMo/Al ₂ O ₃ and NiMo/Al ₂ O ₃ (A3245 at [0020])	Commercial hydroprocessing catalysts including CoMo and NiMo catalysts (A2857 at 2:60-65.)
Pressure	20-150 bar (2-15 MPa) (A3245 at [0020].)	4.8-15.2 MPa (A2858 at 3:1-4.)
Feedstocks listed	Tall oil fatty acid; rapeseed oil; sunflower oil; soybean oil; canola oil; palm oil (A3245 at [0017], A3249 at [0068].)	Tall oil fatty acid; rapeseed oil; sunflower oil; soybean oil; canola oil; palm oil (A2860-2861 at 8:43-10:19.)

(A2172-2173.)

One of ordinary skill would have been drawn to the examples and HDO test results of the prior art as representing actual working conditions, rather than to the general temperature ranges of Jakkula, which did not identify any specific HDO reaction temperature for any particular feedstock. (A2177 at ¶ 67.) Notably, the art

available in 2005 contained no HDO working examples within the claimed range of 280-330 °C. (A2177 at ¶ 67.)

E. Neste's Motion to Amend

Neste's motion to amend proposed to cancel original claims 1-20 and replace them with claims 21-30 to better define the invention and more clearly distinguish it from the prior art discussed above. The motion addressed the knowledge and level of skill of an ordinary artisan in 2005 (A2130), and the patentability of proposed claims 21-30 over the prior art asserted by REG as well as other potentially relevant prior art known to Neste (A2131-2138; A2175-2183). It also set forth how each of the amendments to substitute claims 21-30 distinguished them from the prior art. (A2132-2139.) Each amendment responded to a ground of unpatentability involved in the trial and did not enlarge the scope of the patent claims. 37 C.F.R. § 42.121.

Independent claim 21 incorporated several limitations from the original dependent claims (with additions underlined and deletions struck through):

21. (Substitute for Original Claims 1, 3, 4, and 7) A process for the manufacture of diesel range hydrocarbons comprising:

combining a fresh feed stream of biological origin containing more than 5 wt-% of free fatty acids and a stream of diluting agent containing hydrocarbons of biological origin to form a total feed stream,

introducing the total feed stream to a hydrodeoxygenation step, hydrodeoxygenating the total feed, in the hydrodeoxygenating step, at a reaction temperature between 280-330 °C to form a

hydrodeoxygenated product containing n-paraffins in the diesel range and less than 1 wt-% of high molecular weight hydrocarbons,

introducing the hydrodeoxygenated product to an isomerization step, and isomerizing the hydrodeoxygenated product in the isomerization step to form isoparaffins in the diesel range,

wherein the total feed stream contains less than 40 1 w-ppm alkali and alkaline earth metals, calculated as elemental alkali and alkaline earth metals, less than 40 1 w-ppm other metals, calculated as elemental metals, and less than 30 5 w-ppm phosphorous, calculated as elemental phosphorous.

(A2124.)

Relevant to this appeal, proposed dependent claim 22 included the limitations of claim 21 but also specified a 5-30:1 ratio of diluting agent to fresh feed in the total feed (i.e., a ratio of five to thirty parts diluting agent to one part fresh feed). (A2125.) Thus, claim 22 is narrowly drawn to incorporate the limitations of claim 1 as well as those of claims 3, 4, 5, and 7, which depended from claim 1. (A2124-2126; A66-67 at 16:38-17:4, 17:7-10.)

F. The Board's Decision

The Board's final written decision granted Neste's motion to amend only as to cancelation of claims 1-20. (A28-29.) The Board held proposed claims 21 and 24-30 unpatentable for lack of written description and claims 21-30 unpatentable as obvious in view of the prior art. (A37; A46.)

Proposed claim 22, which is the focus of this appeal, was not held unpatentable on written description grounds. (A37.) Thus, this Court need not address any written description issue. The only issue on appeal concerns whether

the Board erred as a matter of law in concluding that the subject matter of claim 22 would have been obvious.

The Board's obviousness analysis focused on whether two particular limitations—the HDO reaction temperature of 280-330 °C and hydrodeoxygenated product containing less than 1 wt.% of high molecular weight hydrocarbons—rendered the claims patentable. (A38.) It did not address the combined features of claim 22 or the obviousness or nonobviousness of claim 22 as a whole. (A38-47.)

Regarding the HDO temperature issue, the Board stated that, because the proposed 280-330 °C temperature range was fully encompassed by Jakkula's disclosed 200-500 °C range, and partially overlapped the preferred temperature range of 300-400 °C, the claimed range was presumed to be obvious. (A39.) The Board cited *In re Peterson*, 315 F.3d 1325, 1329 (Fed. Cir. 2003), as purportedly supporting a presumption of obviousness in this case. (A39.) It then held that Neste had not carried its burden to rebut that alleged presumption of obviousness, relying principally on Dr. Sughrue's testimony and "Jakkula's disclosed successful results." (A41.)

Regarding the requirement for less than 1 wt.% high molecular weight hydrocarbons, the Board held that Neste had admitted that it was known that free fatty acids contributed to the formation of high molecular weight hydrocarbons; that Example 5 of the '094 patent did not establish that each of the claim

limitations was necessary to achieve an HDO product containing less than 1 wt.% high molecular weight hydrocarbons; and that one of ordinary skill could optimize reaction conditions to minimize the level of high molecular weight hydrocarbons. (A42-45.)

As to claim 22, the Board again addressed a single claim limitation in isolation, crediting Dr. Sughrue's testimony that one of ordinary skill would have been able to determine the optimal dilution ratio while working within the dilution ratios set forth in the prior art. (A45-46.) The Board also held that Neste had not addressed the knowledge, skill, and creativity of an ordinary artisan and did "not address the 'prior art known to the patent owner.'" (A45 (citing *Idle Free Sys. Inc. v. Bergstrom, Inc.*, Case IPR2012-00027, slip. op. at 7 (PTAB June 11, 2013)(Paper 26)).) The Board's decision, however, addressed only the Craig, Jakkula, CZ '575, and Harrison references. The Board did not consider or analyze Monnier, Coxworth, or SE '633, which Neste had asserted supported nonobviousness.

III. SUMMARY OF THE ARGUMENT

Neste presented compelling evidence that the subject matter of proposed claim 22, considered as a whole, would not have been obvious to one of ordinary skill in the art as of the July 2005 priority date. The claimed process for manufacturing diesel-range hydrocarbons has several specific requirements:

- combining a fresh biological feed stream containing more than 5 wt.% free fatty acids and a diluting agent containing hydrocarbons of biological origin to form a total feed in which the ratio of diluting agent to fresh feed in the total feed is 5-30:1;
- hydrodeoxygenating the total feed at a reaction temperature of 280-330 °C to form diesel-range n-paraffins and less than 1 wt.% high molecular weight hydrocarbons;
- isomerizing the hydrodeoxygenated product to form diesel-range isoparaffins;
- in which the total feed contains less than 1 w-ppm alkali and alkaline earth metals, less than 1 w-ppm other metals, and less than 5 w-ppm phosphorous.

The claimed process is the combination of these required elements, yet the Board only considered two individual elements (the HDO temperature and high molecular weight hydrocarbon limitations). This was legal error because a proper obviousness analysis must consider the claim as a whole. Moreover, the Board's legal error was harmful. Claim 22 requires a fresh biological feed stream containing more than 5 wt.% free fatty acids. Neste proved not only that HDO reaction temperatures were understood in July 2005 to be feedstock dependent, but also that *higher* HDO reaction temperatures (further away from the claimed range) were believed to be needed for biological feedstocks containing free fatty acids.

The Board failed to address the feedstock dependence of HDO reaction temperature (which REG did not dispute) and did not even mention the claim requirement for a feedstock containing more than 5 wt.% free fatty acids in analyzing whether the prior art taught away from HDO temperatures in the claimed range. Its obviousness analysis was therefore fundamentally flawed as a matter of law.

In addition, the Board presumed that an HDO temperature of 280-330 °C would have been obvious based on the “overlapping ranges” principle of *In re Peterson*, 315 F.3d 1325 (Fed. Cir. 2003). In *Peterson*, however, the claim listed ranges for several components, each of which fell within the corresponding ranges of a prior art reference. That is not the case here. Claim 22 includes ranges that do not fall within a corresponding prior art range. The Board erred in considering a single claimed range (HDO temperature) in isolation without comparing other claimed ranges or considering the claimed process as a whole.

The Board also disregarded unchallenged evidence that one of ordinary skill would have avoided HDO reaction temperatures within the claimed range. As Dr. Klein testified, Craig concluded from a detailed temperature study that HDO of biological feedstocks at temperatures below 350 °C *did not work* due to reactor plugging. Dr. Sughrue never disputed this key testimony; indeed, his declarations were silent about reactor plugging. The Board cited testimony by Dr. Sughrue

concerning “reactor configuration and operating conditions,” which had nothing to do with the reactor plugging problem. In addition, the Board stated that “in light of Jakkula’s disclosed successful results,” one of ordinary skill would not have viewed Craig’s 350 °C minimum temperature for trouble-free operation as a line not to be crossed. But Jakkula only included experimental results for one HDO example, which did not disclose the HDO temperature used. Thus, Jakkula’s results could not have led one of ordinary skill to select an HDO temperature below 350 °C for biological feedstocks containing more than 5 wt.% free fatty acids. Finally, the Board failed to analyze Monnier and other relevant prior art references that were entirely consistent with Craig’s teaching away from HDO temperatures below 350 °C for biological feedstocks containing more than 5 wt.% free fatty acids. Collectively, these multiple errors demonstrate that the Board’s conclusion of obviousness was incorrect and should be reversed.

IV. ARGUMENT

A. Legal Standards

A claimed invention is unpatentable for obviousness if the differences between it and the prior art “are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art.” 35 U.S.C. § 103(a) (1994); *Graham v. John Deere Co.*, 383 U.S. 1, 14 (1966). Obviousness is a legal question based on underlying factual determinations

including: (1) the scope and content of the prior art; (2) the level of ordinary skill; (3) the differences between the claimed invention and the prior art; and (4) objective evidence of nonobviousness. *Graham*, 383 U.S. at 17-18; *In re Zurko*, 258 F.3d 1379, 1383-84 (Fed. Cir. 2001).

This Court reviews the Board's ultimate legal determination of obviousness without deference. *Zurko*, 258 F.3d at 1384. Factual findings underlying this determination are reviewed for substantial evidence. *Id.*; *In re Giannelli*, 739 F.3d 1375, 1378-79 (Fed. Cir. 2014). Substantial evidence is that quantum of evidence that a reasonable mind might accept as adequately supporting the conclusion for which it is proffered. *See Consolidated Edison Co. v. Nat'l Labor Relations Bd.*, 305 U.S. 197, 229 (1938).

As the party moving to amend the '094 patent, Neste had the burden to establish that the proposed claims were patentable by a preponderance of the evidence. *See* 37 C.F.R. §§ 42.20(c), 42.1(d) (preponderance of the evidence is default evidentiary standard in Board proceedings).

B. The Board Failed to Consider Claim 22 as a Whole or Address the Feedstock Dependence of HDO Reaction Temperature

Proposed claim 22 defines a process for manufacturing diesel-range hydrocarbons by combining a fresh biological feed stream containing more than 5 wt.% free fatty acids and a diluting agent containing hydrocarbons of biological origin to form a total feed in which the ratio of diluting agent to fresh feed in the

total feed is 5-30:1; hydrodeoxygenating the total feed at a reaction temperature of 280-330 °C to form diesel-range n-paraffins and less than 1 wt.% high molecular weight hydrocarbons; and isomerizing the hydrodeoxygenated product to form diesel-range isoparaffins, in which the total feed contains less than 1 w-ppm alkali and alkaline earth metals, less than 1 w-ppm other metals, and less than 5 w-ppm phosphorous. (*Supra* Part II.E.) The claimed process requires this particular combination of elements.

The Board, however, focused only on whether two individual claim limitations rendered the claims patentable. (*Supra* Part II.F; A38.) Separately addressing only the HDO reaction temperature of 280-330 °C and the less than 1 wt.% of high molecular weight hydrocarbons claim limitations, the Board did not analyze or make any findings regarding the combined features of claim 22 or the obviousness or nonobviousness of claim 22 as a whole. (*Supra* Part II.F; A38.)

This was legal error. It is axiomatic that, under *Graham*, obviousness must be analyzed as to the claim as a whole. *CFMT, Inc. v. Yieldup Int'l. Corp.*, 349 F.3d 1333, 1342 (Fed. Cir. 2003) (“obviousness requires a suggestion of all limitations in a claim”) (citing *In re Royka*, 490 F.2d 981, 985 (C.C.P.A. 1974)). The inquiry is highly fact-specific by design. *In re Brouwer*, 77 F.3d 422, 425 (Fed. Cir. 1996). Failure to follow the *Graham* analysis can consequently require reversal. *In re Pardo*, 684 F.2d 912, 917 (C.C.P.A. 1982). Despite these

requirements, the Board never conducted a proper *Graham* analysis of claim 22 as a whole. To the contrary, it disregarded all but two claim limitations. (*Supra* Part II.F.) Thus, the Board's obviousness conclusion should be reversed.

In *In re Wilson*, for example, the Board disregarded the claim term "incompatible." 424 F.2d 1382, 1385 (C.C.P.A. 1970). Believing the term "too relative" but not rejecting the claim as indefinite, the Board ignored the term, proceeding as though it was not part of the claims. *Id.* But, as this Court held, "[a]ll words in a claim must be considered in judging the patentability of that claim against the prior art." *Id.* The Court therefore reversed the Board's unsupported obviousness ruling. *Id.*

Similarly, the Court reversed the Board's obviousness ruling in *In re De La Chevrelie* because the Board disregarded a critical claim limitation. 485 F.2d 1403, 1407 (C.C.P.A. 1973). In *De La Chevrelie*, the invention related to an automated system for soil irrigation. *Id.* at 1404. The claim specifically required placing one electrode in a permanently moist zone, which the specification described as lying below root depth. *Id.* at 1407. The prior art did not discuss the existence of a permanently moist zone, only suggesting locating the electrodes down to root depth. *Id.* Because the Board ignored the critical claim limitation relating to electrode placement, the Court reversed the obviousness ruling. *Id.*

Here, the Board disregarded all but two claim limitations, committing legal error as in *Wilson* and *De La Chevrelie*.

Moreover, the Board's legal error was harmful. Claim 22 specifically requires a fresh biological feed stream containing more than 5 wt.% free fatty acids, and Neste proved that one of ordinary skill would have understood from Craig that HDO reaction temperature is feedstock dependent. (*Supra* Parts II.D.1, II.E.) Dr. Sughrue never disputed this key point. (*Supra* Part II.D.1.) For tall oil fatty acid, which contains more than 5 wt.% free fatty acids, Craig describes an HDO temperature of 380-450 °C with an optimum temperature of 390 °C. (*Supra* Part II.D.1; A2860-2861 at Table 8; A2862 at 12:30-34; A2210 at ¶ 29.) Tall oil fatty acid (containing free fatty acids) was therefore "processed at somewhat *higher* temperatures than that utilized for the vegetable oils." (A2861 at 9:38-10:19 (emphasis added); *see supra* Part II.D.1.) Monnier also specifically addresses the HDO of biological feedstocks containing more than 5 wt.% free fatty acids and describes reaction temperatures of at least 350 °C and working examples at 370-410 °C for these feedstocks. (A2211 at ¶ 31; A2212-2213 at ¶ 32; A2664 at 2:56-58.)

The Board, however, failed to address the feedstock dependence of HDO reaction temperature in its decision. (*Supra* Part II.F; A37-47.) Indeed, it did not even mention the requirement of claim 22 for a feedstock containing more than 5

wt.% free fatty acids in analyzing whether the prior art taught away from HDO temperatures in the claimed range (280-330 °C). (*Supra* Part II.F; A39-42.) The issue, however, was not whether it would have been obvious to select an HDO reaction temperature in the claimed range in the abstract or in general, but whether it would have been obvious to do so in the overall claimed process *with a biological feedstock containing more than 5 wt.% free fatty acids*. Because the Board failed to consider claim 22 as a whole, it never addressed this issue and thus its obviousness analysis was legally erroneous and should be reversed. *Wilson*, 424 F.2d at 1385; *De La Chevrelire*, 485 F.2d at 1407.

C. The Board Erred in Concluding that the Prior Art Did Not Teach Away from the Claimed HDO Reaction Temperatures

The Board presumed that the claimed 280-330 °C temperature range would have been obvious because Jakkula's disclosed temperature ranges fully encompass or partially overlap the claimed range. (*Supra* Part II.F; A39 (citing *In re Peterson*, 315 F.3d 1325, 1329 (Fed. Cir. 2003)).) But having failed to consider claim 22 as a whole, the Board misapplied the overlapping range principle of *Peterson*. Rather than supporting a *prima facie* case or presumption of obviousness, *Peterson* supports the opposite conclusion.

The *Peterson* claims, directed to super-alloys, recited percent ranges for ten metals, including chromium and rhenium. *Peterson*, 315 F.3d at 1329. Comparing (in a table) the claimed ranges to the ranges disclosed in a prior art reference

(Shah), the Court determined that they had overlapping ranges “*as each range listed in . . . claim 5 lies within the corresponding range disclosed in Shah.*” *Id.* (emphasis added); *see also In re Patel*, 566 Fed. App’x 1005, 1010 (Fed. Cir. 2014) (non-precedential) (noting for remand that “all of the ranges in *In re Peterson* overlapped at least to some degree”).

Here, the Board applied *Peterson*’s overlapping range principle to a single claimed range (the 280-330 °C HDO temperature range) in isolation without comparing other claimed ranges or considering the claimed process as a whole. Unlike the completely overlapping set of ranges in *Peterson*, claim 22 includes ranges that do not fall within a corresponding prior art range. Jakkula and Harrison, for example, do not mention levels of high molecular weight hydrocarbons, or concentrations of alkali and alkaline earth metals, other metals, and phosphorus (*supra* Parts II.D.4-5), whereas claim 22 specifies particular ranges for those required claim elements (*supra* Part II.E). The Board therefore erred in presuming obviousness based on *Peterson*.

Even if the Board correctly presumed a *prima facie* case of obviousness, however, Neste *rebutted* any such presumption with compelling—and essentially unchallenged—evidence that the prior art taught away from HDO reaction temperatures in the claimed range. *Iron Grip Barbell Co. v. USA Sports, Inc.*, 392 F.3d 1317, 1321 (Fed. Cir. 2004) (presumption of obviousness may be rebutted by

showing that the prior art taught away from the claimed invention). The Board erred in concluding that the prior art did not teach away from the required HDO reaction temperatures.

1. The Board Disregarded Unchallenged Evidence Regarding Craig’s Teaching of Reactor Plugging at HDO Temperatures Below 350 °C

Based on a detailed series of HDO experiments, Craig concluded that “350° C. was the *lower limit* for trouble free operation” and that “[a]t temperatures of 350° C. and lower, the product collection system *was plugged* with a solid margarine-like material” (emphasis added). (*Supra* Part II.D.1.) Craig also found that, at temperatures up to 320 °C, non-suitable solid or semi-solid materials were formed. (*Supra* Part II.D.1.) As Dr. Klein explained, Craig’s statements and experimental results showed that HDO of biological feedstocks *did not work* at temperatures below 350° C due to reactor plugging, which would have discouraged one of ordinary skill from using HDO temperatures within the claimed range. (*Supra* Part II.D; A2172 at ¶ 56.) This is therefore not a case where the prior art merely discloses that higher temperatures are a particularly preferred embodiment or a better alternative. *See, e.g., In re Mouttet*, 686 F.3d 1322, 1333-34 (Fed. Cir. 2012). Instead, the art teaches that temperatures below 350 °C will not work. (A2172 at ¶ 56; A2173 at ¶ 58; A2210 at ¶ 29.) This type of inoperability is the

touchstone of teaching away. *See, e.g., In re Gurley*, 27 F.3d 551, 553 (Fed. Cir. 1994).

A reference teaches away if it leads in a direction divergent from that taken by the claimed invention. *See Teva Pharm. USA, Inc. v. Sandoz, Inc.*, 723 F.3d 1363, 1372-73 (Fed. Cir. 2013), *vacated on other grounds*, No. 13-854, slip op. at 16 (Jan. 20, 2015). In *Teva*, for example, this Court affirmed a finding that claims directed to copolymers having molecular weights of about 5 to 9 kDa were nonobvious because the prior art disclosed copolymers with molecular weights higher than 10 kDa (preferably 18-20 kDa) and stated that molecular weights below 17 kDa were ineffective. *Teva*, 723 F.3d at 1372. The facts here are analogous because both Craig and Monnier describe HDO temperatures above 350 °C for feedstocks containing more than 5 wt.% free fatty acids, with all working examples operating well above 350 °C, and Craig discloses that temperatures below 350 °C will be ineffective. (*Supra* Parts II.D.1-2.)

In rejecting Neste's evidence of teaching away, the Board relied heavily on Dr. Sughrue's testimony as allegedly rebutting Dr. Klein's expert opinions. (*Supra* Part II.F; A41.) But a careful examination of the testimony cited on page 15 of the Board's decision shows that Dr. Sughrue said ***nothing*** about reactor plugging (the word "plug" or "plugging" not even appearing in his declaration). (*Supra* Part II.D.1.) Thus, even if accepted as true, his opinions could not have rebutted Dr.

Klein's testimony that reactor plugging at temperatures below 350 °C meant that HDO at those temperatures would not work. Dr. Sughrue's testimony is discussed in detail below:

Ex. 1040 ¶ 36: Dr. Sughrue stated that one of ordinary skill would not have been dissuaded from considering temperatures in the range of 300-400 °C because model compound studies used temperatures near 300 °C and limitations existed in Craig's ability to measure and report absolute temperatures. (A2689 at ¶ 36.) But nothing in Dr. Sughrue's testimony regarding model compounds using low temperatures addressed Craig's teaching of reactor plugging at temperatures below 350 °C. (*Supra* Part II.D.1.) "Model" compounds, which are single components or simple two- or three-component mixtures with low carbon numbers, are distinct from the complex higher carbon number mixtures of triglycerides and fatty acids that the claimed fresh feed stream of biological origin would contain. (*Supra* Part II.B.) Based on the feedstock sensitivity of HDO temperatures, the low reaction temperatures used for model compounds would not change Craig's disclosure that HDO temperatures below 350 °C would not work for feeds such as that recited in claim 22. (A2221-2228 at ¶¶ 46-58.) The low temperatures of these model compounds in fact only further demonstrate the feedstock dependency of HDO temperatures. (*See* A2226 at ¶ 52; A2228 at ¶ 57.)

Dr. Sughrue also stated that different reactor configurations and catalysts would lead to different *optimal* temperatures from those reported in Craig, in particular to lower temperatures for commercial-scale reactors and for more active NiMo catalysts. (A2689 at ¶ 36.) He further stated that, because Jakkula and CZ '575 were published after Craig and both disclose HDO temperatures lower than Craig's preferred HDO temperature, the timing of these references further evidenced that Craig fails to teach away from lower temperatures. (A2689 at ¶ 36.) But nothing in Dr. Sughrue's testimony addressed Craig's teaching of reactor plugging at temperatures below 350 °C. (*Supra* Part II.D.1.) He never testified, for example, that different reactor configurations or catalysts would avoid reactor plugging or that one of ordinary skill would have known how to avoid reactor plugging at lower HDO temperatures with different reactor configurations or catalysts. Nor did he disagree with Dr. Klein's opinion that Craig's reactor plugging problem was so severe that one of ordinary skill would have understood that HDO *did not work* at temperatures below 350 °C.

Ex. 1040 ¶¶ 31, 33: Dr. Sughrue stated that catalyst activity may influence HDO reactor temperature and that the activity of hydroprocessing catalysts increased dramatically during the 1990s and early 2000s. (A2686 at ¶ 31; A2687 at ¶ 33.) He identified one example of an improved catalyst for hydrodesulfurization (not HDO), which he said showed a 20 °C temperature advantage over a NiMo

catalyst. (A2687 at ¶ 33.) But he did not discuss Craig's reactor plugging problem or attempt to link his opinions on improvements in catalyst activity to any ability of one of ordinary skill to solve that reactor plugging problem. Moreover, neither a 20 °C nor a 25 °C temperature drop in the range of Craig for tall oil fatty acid, or the range of Monnier, would result in a reaction temperature of 280-330 °C. (A2220-2221 at ¶ 44; A2860-2861 at Table 8; A2664 at 2:56-58.)

Ex. 1040 ¶ 37: Dr. Sughrue stated that a person of ordinary skill would have used lower temperatures to avoid side reactions in general and would not have been dissuaded from considering HDO reaction temperatures at or near the low end of the temperature ranges taught by Jakkula. (A2689 at ¶ 37.) But once again, this testimony, which the Board relied upon, had nothing to do with and fails to address Craig's disclosed reactor plugging problem at HDO temperatures below 350 °C. Dr. Sughrue did not establish any connection between these side reactions and the plugging problem identified in Craig.

Ex. 1040 ¶ 42: Dr. Sughrue stated that the dimerization and oligomerization of free fatty acids are relatively strongly dependent on their concentration in the reaction medium, which would have suggested that dilution of the feed stream should reduce the rate of these reactions compared to competing reactions such as HDO. (A2693 at ¶ 42.) Again, he said nothing about reactor plugging. He did not,

for example, link Craig's reactor plugging problem to the dimerization or oligomerization of free fatty acids.

Ex. 1040 ¶ 60: Dr. Sughrue stated that one of ordinary skill would have appreciated that free fatty acids in a feed stream promote the formation of high molecular weight hydrocarbons; that temperature would affect the propensity for such reactions to occur; and that because dimerization and oligomerization were known to be second-order reactions, one of ordinary skill would have appreciated that lowering the concentration of free fatty acids via dilution would decrease the dimerization reactions leading to high molecular weight hydrocarbons. (A2705 at ¶ 60.) But, again, he said nothing about Craig's reactor plugging problem and did not link the formation of high molecular weight hydrocarbons to that reactor plugging.

Ex. 1040 ¶ 90: Dr. Sughrue stated that the allegedly surprising results of the invention were expected. (A2722-2723 at ¶ 90.) He reiterated that because free fatty acid dimerization reactions are second order, one of ordinary skill would have appreciated that dilution would suppress them. (A2722 at ¶ 90.) He also argued that Figure 5 of the '094 patent illustrates that a combination of low HDO temperature, dilution, and feeds having low impurities is not necessary to achieve a low level of high molecular weight hydrocarbons. (A2722-2723 at ¶ 90.) He asserted that one of ordinary skill could have optimized within the temperature

ranges and dilution ratios of the prior art to minimize high molecular weight hydrocarbons. (A2723 at ¶ 90.) But, again, nothing in this testimony addressed Craig's reactor plugging problem at low HDO temperatures or attempted to link the formation of high molecular weight hydrocarbons to reactor plugging.

The Board appears to dismiss Craig's teaching away from temperatures below 350 °C because Craig allegedly did not use directly comparable techniques to Jakkula. (A40-41.) The Board cited the *Young* decision, where the reference that allegedly taught away from the invention did not duplicate or appropriately model the spacing or type of charge used in the primary prior art reference and therefore was afforded little weight. *In re Young*, 927 F.2d 588, 590-92 (Fed. Cir. 1991). In contrast, however, Craig provides actual experimental data for similar HDO processes using similar feedstocks, pressures, and catalysts to Jakkula. (*Supra* Part II.D.5.) Although the Board states that Jakkula uses different reactor configurations and catalysts (A40), Jakkula and Craig both use CoMo and NiMo catalysts and neither Dr. Sughrue nor the Board identified any difference in reactor configuration or how any such difference would avoid reactor plugging. (A39-42; A2686 at ¶ 31; A2687 at ¶ 33; A2689 at ¶¶ 36-37; A2693 at ¶ 42; A2705 at ¶ 60; A2722-2723 at ¶ 90.) In fact, Dr. Sughrue stated he did not believe that Craig's reactor configuration "would cause any difference in [Craig's] conclusions or in [Craig's] results." (A2908-2910 at 46:20-48:3; A2940 at 78:5-10; A2941 at

79:2-15; A2219-2220 at ¶ 43.) The example in Jakkula does not even disclose the reactor configuration for the HDO step. (A3249-3250 at [0068]-[0070].)

Moreover, even though Craig did not study dilution as an operating variable, any difference between the product recycle of Jakkula and Craig would not have been expected to affect the choice of reactor operating temperature, which is a different issue from controlling the reaction heat generated by a reaction. (*Supra* Part II.A; A2215-2220 at ¶¶ 36-43; A2152 at ¶ 20; A2173 at ¶ 59; A3358.) Although the Board cited portions of Dr. Sughrue's declaration in which he asserted that dilution would suppress the creation of high molecular weight hydrocarbons, Dr. Sughrue did *not* state that dilution would solve Craig's reactor plugging problem. (A2686 at ¶ 31; A2687 at ¶ 33; A2689 at ¶¶ 36-37; A2693 at ¶ 42; A2705 at ¶ 60; A2722-2723 at ¶ 90.)

Not only is the cited Sughrue testimony entirely non-responsive to Neste's evidence of expected reactor plugging at low HDO temperatures, but Dr. Sughrue also cites little or no evidence or scientific facts to support his opinions in the portions of his expert declaration relied upon by the Board, summarized above. (*See* A2686 at ¶ 31; A2687 at ¶ 33; A2689 at ¶¶ 36-37; A2693 at ¶ 42; A2705 at ¶ 60; A2722-2723 at ¶ 90.) Consequently, even if his opinions were relevant to the teaching away issue (which they are not), the Board erred in relying on such conclusory expert opinions unsupported by additional facts. *Upjohn Co. v. Mova*

Pharm. Corp., 225 F.3d 1306, 1311 (Fed. Cir. 2000) (holding that record lacked substantial evidence in support of technical expert's conclusion of obviousness). Dr. Sughrue's testimony thus provided no reasoned basis to disregard the explicit teachings of Craig or Dr. Klein's expert testimony that one of ordinary skill would have avoided HDO temperatures below 350 °C for biological feedstocks containing more than 5 wt.% free fatty acids because Craig taught they did not work due to reactor plugging. (*See* A39-42.)

2. The Board Misinterpreted Jakkula's Successful Results

The Board also held that, "in light of Jakkula's disclosed successful results," one of ordinary skill would not have viewed Craig's 350 °C minimum temperature for trouble-free operation as a line not to be crossed, but would have understood that the optimal and minimum temperatures for HDO would vary depending on the particular reactor configuration and operating conditions used. (A41.) The Board similarly observed that Jakkula reported no issues with reactor plugging. (A39.)

But Jakkula simply discloses a general range of HDO temperatures for a broad variety of biological feedstocks and does not recommend any particular HDO temperature for any specific feedstock. (*Supra* Part II.D.5.) Moreover, Jakkula includes only one HDO working example (using a tall oil fatty acid feedstock), but ***does not disclose the HDO temperature used*** in that example. (*Supra* Part II.D.5.) One of ordinary skill could not have logically concluded from

this example (or any other portion of Jakkula) that lower HDO temperatures within the claimed range would not cause reactor plugging. No evidence exists that Jakkula succeeded at processing a tall oil fatty acid (TOFA) feedstock containing high amounts of free fatty acids at temperatures within the claimed range. Thus, although the experimental results in Jakkula may have been “successful,” as the Board stated, the HDO temperature was not disclosed and therefore Jakkula’s results would have been uninformative to one of ordinary skill. Indeed, one of ordinary skill would have simply assumed that Jakkula used a conventional high HDO temperature with the tall oil fatty acid feedstock. (A2210-2211 at ¶ 30.)

Interpreting Jakkula as disclosing successful results at the low HDO temperatures claimed with a feedstock containing more than 5 wt.% free fatty acids would be an extremely strained interpretation of the reference, which could only be made in hindsight. *In re Hedges*, 783 F.2d 1038, 1041 (Fed. Cir. 1986) (citing *In re Rosenberger*, 386 F.2d 1015, 1018 (C.C.P.A. 1967)).

3. The Board Failed to Analyze Monnier and Other Relevant Prior Art

A proper obviousness inquiry considers the teachings of the prior art as a whole. *Hedges*, 783 F.2d at 1041; *see also* M.P.E.P. § 2141.02 (requiring analysis of “both the invention and prior art as a whole”). It is impermissible to exclude prior art that is necessary to fully appreciate what one of ordinary skill in the art would have considered. *See Hedges*, 783 F.2d at 1041. Here, compounding its

erroneous analysis of the HDO temperature issue, the Board failed to analyze prior art references that support nonobviousness, including Monnier, Coxworth, and SE '633. (A37-47.)

In *Hedges*, this Court reversed the U.S. Patent and Trademark Office's obviousness decision because the prior art *as a whole* taught away from the high temperatures required in the claimed process of sulfonating diphenyl sulfone. *Hedges*, 783 F.2d at 1041. The USPTO had held the claims obvious over a prior art reference disclosing low sulfonating temperatures with no upper limit, finding that one could have determined optimum temperature through routine experimentation. *Id.* at 1039-40. Considering the prior art as a whole, however, this Court determined that all the references suggested lower reaction temperatures with no reference suggesting that diphenyl sulfate could be advantageously reacted at the high temperatures claimed. *Id.* at 1040-41. Further, the Court agreed with the applicant that the prior art taught that charring and decomposition would be expected at high temperatures. *See id.* Based on the teachings of the prior art as a whole, the Court concluded that the applicant's claim of a high reaction temperature was contrary to the accepted wisdom in the art to use low temperatures and therefore reversed the PTO's conclusion of obviousness. *Id.*

In this case, similar to *Hedges*, even though Jakkula teaches a broad, general HDO temperature range, the prior art as a whole consistently teaches high HDO

temperatures for feedstocks containing more than 5 wt.% free fatty acids. (*Supra* Part II.D.) No reference suggests or discloses examples of HDO of such feedstocks at the low 280-330 °C temperature range claimed, and Craig discloses reactor plugging at temperatures below 350 °C. (*Supra* Part II.D.) Monnier specifically describes the HDO of biological feedstocks containing free fatty acids, disclosing reaction temperatures of at least 350 °C and working examples at 370-410 °C. (*Supra* Part II.D.2.) These HDO reaction temperatures are entirely consistent with Craig's similar temperatures and would have further led away from the claimed HDO temperature of 280-330 °C for feedstocks containing more than 5 wt.% free fatty acids. (*Supra* Part II.D.2.) Yet the Board made no findings as to Monnier and did not even mention this highly relevant prior art reference in its decision. (A37-47.)

Other prior art references, including Coxworth, CZ '575, and SE '633, also describe working examples with HDO temperatures well above the claimed range of 280-330 °C. (*Supra* Part II.D.2-3; A2178.) The Board, however, did not address any of them in its analysis of HDO temperature, only briefly mentioning the disclosure of dilution ratios in CZ '575. (A37-47.) Nor did it address the fact that no prior art reference disclosed any working example within the claimed HDO temperature range. (A37-47.) Viewing the prior art as a whole shows that a 280-330 °C HDO temperature range for feedstocks containing more than 5 wt.%

free fatty acids was contrary to accepted wisdom and would have been nonobvious. *Hedges*, 783 F.2d at 1040-41. For all these reasons, the Board's determination that the prior art did not teach away is erroneous, providing further basis to reverse the obviousness decision. *Id.*; see also *Crocs, Inc. v. ITC*, 598 F.3d 1294, 1308-09, 1311 (Fed. Cir. 2010).

D. Considered as a Whole, the Invention of Claim 22 Would Not Have Been Obvious Absent Hindsight

The '094 patent discloses a process for converting biological feedstocks containing more than 5 wt.% free fatty acids into diesel-range n-paraffins with minimal formation of undesired high molecular weight hydrocarbons (less than 1 wt.%). (*Supra* Part II.C.) The process of claim 22 uses a reduced HDO reaction temperature (280-330 °C) compared to the prior art; low levels of contaminants in the total feed (less than 1 w-ppm alkali and alkaline earth metals, less than 1 w-ppm other metals, and less than 5 w-ppm phosphorous); and a 5-30:1 ratio of diluting agent to fresh feed in the total feed. (*Supra* Parts II.D-E.)

Claim 22 is reasonable in scope and embodies the inventors' discoveries reflected in the specification, including in the series of experiments described in the examples. The Board criticized one of those examples, Example 5, as allegedly not establishing that each claim limitation is needed to achieve an HDO product with less than 1 wt.% high molecular weight hydrocarbons or that one of ordinary skill could not optimize reaction conditions to minimize high molecular weight

hydrocarbons without the disclosure of the '094 patent. (A44-45.) The invention, however, was based on the *overall* series of experiments described in the specification (*supra* Part II.C), which the Board never addressed. Example 5 and the other examples simply illustrate the invention; they do not limit it. Moreover, the question of whether one of ordinary skill could have reduced high molecular weight hydrocarbons without using the claimed process has nothing to do with whether the claimed process would have been *obvious*.

In holding claim 22 obvious, the Board relied primarily on Jakkula. Yet Jakkula does not disclose an HDO product containing less than 1 wt.% of high molecular weight hydrocarbons. (*Supra* Part II.D.5.) To the contrary, Jakkula provides no compositional information for its HDO product. (*Supra* Part II.D.5.) Jakkula also does not disclose the contaminant levels of its total feed stream or the reaction temperature used in its single HDO working example. (*Supra* Part II.D.5.) Jakkula therefore fails to suggest that one could produce n-paraffins with less than 1 wt.% high molecular weight hydrocarbons from biological feedstocks containing more than 5 wt.% free fatty acids by combining a low HDO reaction temperature (280-330 °C) with the specified low levels of contaminants in the total feed and a 5-30:1 ratio of diluting agent to fresh feed in the total feed.

The Board also relied on Harrison, a general reference not specific to any particular type of hydrogenation. (*Supra* Part II.D.4.) Harrison does not identify

any HDO temperature, only describing preferred temperatures for hydrodesulfurization. (*Supra* Part II.D.4.) As such, it also fails to suggest any specific HDO temperature for feedstocks having more than 5 wt.% free fatty acids.

Craig and other prior art are patentably distinguishable for the reasons given above. Nothing in the prior art suggests the claimed process as a whole. Contrary to the Board's assertion that Neste did not address known prior art, Neste's expert Dr. Klein analyzed and discussed not only the voluminous references cited by REG in its asserted grounds of unpatentability, but several additional prior art references other than those cited by REG. (*See, e.g.*, A2175-2183 at ¶¶ 65, 73, 75, 76; A2135-2136.) None of those references described or suggested the process of claim 22. (*Id.*)

Only through hindsight reconstruction of the claimed invention would claim 22 have been obvious. But hindsight bias remains a legally improper mode of obviousness analysis. *Mintz v. Dietz & Watson, Inc.*, 679 F.3d 1372, 1377 (Fed. Cir. 2012) (noting "prohibited reliance on hindsight"); *In re NTP, Inc.*, 654 F.3d 1279, 1299 (Fed. Cir. 2011) (reversing Board's obviousness ruling because it was "based on improper hindsight reasoning").

V. CONCLUSION

Proposed claim 22 is patentable over the prior art for the reasons detailed above. The Board's decision holding claim 22 unpatentable on obviousness grounds is legally erroneous and factually unsupported and should be reversed.

Respectfully submitted,

Date: January 21, 2015

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ADDENDUM

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Paper 63
Entered: August 29, 2014

UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE PATENT TRIAL AND APPEAL BOARD

REG SYNTHETIC FUELS, LLC,¹
Petitioner,

v.

NESTE OIL OYJ,
Patent Owner.

Case IPR2013-00178
Patent 8,212,094 B2

Before RAMA G. ELLURU, CHRISTOPHER L. CRUMBLEY, and
JON B. TORNQUIST, *Administrative Patent Judges*.

TORNQUIST, *Administrative Patent Judge*.

FINAL WRITTEN DECISION
35 U.S.C. § 318(a) and 37 C.F.R. § 42.73

¹ On June 24, 2014, REG Synthetic Fuels, LLC (“REG”) filed updated Mandatory Notices informing the Board that it had acquired—and is the successor-in-interest to—Syntroleum Corporation, the originally-named Petitioner in this proceeding. Paper 62. REG also filed a Power of Attorney on that date, retaining the same counsel that filed the Petition on behalf of Syntroleum. Paper 61.

IPR2013-00178
Patent 8,212,094 B2

I. BACKGROUND

On March 8, 2013, Syntroleum Corp. (“Petitioner”) filed a Petition for *inter partes* review of claims 1–20 of U.S. Patent No. 8,212,094 B2 (Ex. 1001, “the ’094 patent”). On March 21, 2013, Petitioner filed a corrected Petition. (Paper 7, “Pet.”). On June 14, 2013, Nestle Oil Oyj (“Patent Owner”) filed a Preliminary Response (Paper 11, “Prelim. Resp.”). In a Decision to Institute (Paper 22, “Dec. on Inst.”) issued September 4, 2013, we instituted an *inter partes* review of claims 1–20 of the ’094 patent.

Patent Owner did not file a Patent Owner Response, and chose instead to file a Motion to Amend (Paper 38, “Mot.”). Petitioner filed an Opposition to the Motion to Amend (Paper 42, “Opp.”), and Patent Owner filed a Reply (Paper 46, “PO Reply”). We held an oral hearing on April 1, 2014, and a transcript of the oral hearing (Paper 60, “Tr.”) is included in the record.

Both Petitioner and Patent Owner presented declaration testimony in support of their respective positions. With its Petition, Petitioner provided a declaration from Edward L. Sughrue II, PhD. (Ex. 1002). With its Motion to Amend, Patent Owner provided a declaration from Michael T. Klein, Sc.D. (Ex. 2019). With its Opposition, Petitioner provided a second declaration from Dr. Sughrue (Ex. 1040), and with its Reply, Patent Owner provided a second declaration from Dr. Klein (Ex. 2041).

We have jurisdiction under 35 U.S.C. § 6(c). This final written decision, issued pursuant to 35 U.S.C. § 318(a) and 37 C.F.R. § 42.73, addresses issues raised during trial.

In its Motion to Amend, Patent Owner requests cancellation of claims 1–20 and substitution of those claims with proposed claims 21–30. For the reasons discussed below, we determine that Patent Owner has not met its burden to prove

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by a preponderance of the evidence that the proposed substitute claims are patentable. Accordingly, Patent Owner's Motion to Amend is *granted* with respect to the cancellation of claims 1–20 and *denied* with respect to the substitution of claims 21–30.

A. *The '094 Patent*

The '094 patent relates to a process for the manufacture of diesel range hydrocarbons from renewable sources, such as plant and animal oils or fats. Ex. 1001, 5:22–24. In the '094 patent, a two-step process comprising a hydrodeoxygenation, or HDO, step and an isomerization step is used to convert the fatty acids and fatty acid derivatives in the fresh feed stream into branched n-paraffin reaction products suitable for blending with diesel fuel. *Id.* at 5:22–39, 6:27–30, 10:8–20. In the HDO step, a stream of hydrogen and fresh feed is introduced on catalyst beds. *Id.* at 6:17–24. As the hydrogen and fresh feed pass over the catalyst beds, “oxygen from organic oxygen compounds” is removed as water. *Id.* at 4:48–50. “[I]n the isomerization step, isomerization is carried out which causes branching of the hydrocarbon chain and results in improved performance of the product oil at low temperatures.” *Id.* at 10:9–13.

In the process of the '094 patent, the HDO step is performed at a “temperature between 200 and 400 °C, preferably between 250 and 350 °C, and most preferably between 280 and 340 °C.” *Id.* at 9:4–8. Because the HDO step is highly exothermic, a hydrocarbon diluting agent is introduced during the HDO step to limit the temperature rise in the reactor. *Id.* at 1:66–2:8, 5:65–6:7. The diluting agent may be a separate hydrocarbon or recycled product from the HDO step that has been cooled using a heat exchanger. *Id.* at 6:42–48, 7:13–16. “[T]he ratio of the dilution agent/fresh feed is 5-30:1, preferably 10-30:1, most preferably 12-25:1.” *Id.* at 8:65–67.

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B. Instituted Challenges

In the Decision to Institute, we considered Petitioner's and Patent Owner's arguments for and against the patentability of claims 1–20 and instituted *inter partes* review of the '094 patent on the following grounds:

- 1) Claims 1, 4, 7, and 9–20 as anticipated by Jakkula;²
- 2) Claims 1–7 and 9–20 as having been obvious over Jakkula;
- 3) Claim 8 as having been obvious over Jakkula and Monnier;³ and
- 4) Claims 5 and 6 as having been obvious over Jakkula and Harrison.⁴

Dec. on Inst. 24.

Patent Owner did not file a Patent Owner response addressing the patentability of claims 1–20, nor did Patent Owner provide additional reasoning or argument to support the patentability of these claims in the Motion to Amend.

C. Illustrative Claims

In its Motion to Amend, Patent Owner proposes to add substitute claims 21–30. Mot. 2. Substitute claims 21 and 30 are illustrative of the proposed substitute claims and are reproduced below:⁵

21. (Substitute for Original Claims 1, 3, 4, and 7) A process for the manufacture of diesel range hydrocarbons comprising:

combining a fresh feed stream of biological origin containing more than 5 wt-% of free fatty acids and a stream of diluting agent containing hydrocarbons of biological origin to form a total feed stream,

² EP Pub. App. 1396531 A2 (Ex. 1006) (“Jakkula”).

³ U.S. Patent No. 5,705,722 (Ex. 1031) (“Monnier”).

⁴ U.S. Patent No. 5,093,535 (Ex. 1014) (“Harrison”).

⁵ Subject matter deleted from original claim 1 is enclosed by brackets; subject matter added to that claim is underlined.

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introducing the total feed stream to a hydrodeoxygenation step, hydrodeoxygenating the total feed, in the hydrodeoxygenating step, at a reaction temperature between 280-330 °C to form a hydrodeoxygenated product containing n-paraffins in the diesel range and less than 1 wt-% of high molecular weight hydrocarbons,

introducing the hydrodeoxygenated product to an isomerization step, and isomerizing the hydrodeoxygenated product in the isomerization step to form isoparaffins in the diesel range,

wherein the total feed stream contains less than [10] 1 w-ppm alkali and alkaline earth metals, calculated as elemental alkali and alkaline earth metals, less than [10] 1 w-ppm other metals, calculated as elemental metals, and less than [30] 5 w-ppm phosphorous, calculated as elemental phosphorous.

30. (New) The process according to claim 21, wherein the hydrodeoxygenating step is at a reaction temperature between 280-305 °C.

Dependent claims 22–29 are proposed substitutes for original claims 5, 6, and 8–13 of the '094 patent. Mot. 4–5. These proposed substitute claims differ from the original claims only in that they recite dependency from newly proposed claim 21, instead of original claim 1. *Id.*

II. DISCUSSION

A. *Claim Construction*

Neither party challenges the claim constructions provided in the Decision to Institute. Accordingly, to the extent that they are necessary for assessing Patent Owner's Motion to Amend, those previous constructions are adopted for purposes of this final decision. *See* Dec. on Inst. 8–13.

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With respect to the newly added limitations, Patent Owner submits proposed constructions for the terms: *reaction temperature*, *n-paraffins*, *high molecular weight hydrocarbons*, and *isoparaffins*. Mot. 7–8.

1. *Isoparaffins and n-Paraffins*

Patent Owner argues that *isoparaffins* “should be construed to mean alkanes having one or more C1-C9, typically C1-C2 alkyl side chains, typically mono-, di-, tri-, or tetramethylalkanes” and *n-paraffins* “should be construed to mean normal alkanes or linear alkanes that do not contain side chains.” Mot. 8. Petitioner does not dispute these proposed constructions. As Patent Owner’s proposed constructions mirror the express definitions provided in the patent, we construe the terms in a manner consistent with Patent Owner’s proposals. *See* Ex. 1001, 5:12–16.

2. *Reaction Temperature and High Molecular Weight Hydrocarbons*

Patent Owner asserts that *reaction temperature* should be construed to mean “the temperature at which a hydrodeoxygenation reaction occurs” and *high molecular weight hydrocarbons* should be construed to mean “hydrocarbons having a molecular weight double or more of the feed,” which “are not in the boiling range of diesel fuel.” Mot. 8; Ex. 2019 ¶¶ 36, 38. In its Opposition, Petitioner asserts that *reaction temperature* should be construed as the “temperature of the HDO reactor” and that the term *high molecular weight hydrocarbons* is indefinite. Opp. 1.

At oral argument the parties conceded that their respective written description and patentability arguments did not rely on the construction of either term. Tr. 8:10–17, 11:12–20, 61:2–9, 62:19–63:3. As our decision in this case, likewise, does not turn on a particular construction for these terms,

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we decline to provide an express construction for *reaction temperature* and *high molecular weight hydrocarbons*.

B. The Motion to Amend

An *inter partes* review is more adjudicatory than examinational. *See generally Abbott Labs. v. Cordis Corp.*, 710 F.3d 1318, 1326 (Fed. Cir. 2013). Unlike examination, entry of the proposed substitute claims in an *inter partes* review is not automatic. Patent Owner must establish that it is entitled to the requested relief. *See* 37 C.F.R. § 42.20(c).

In its Motion to Amend, Patent Owner bears the burden to show, *inter alia*, that a reasonable number of substitute claims are proposed, that these claims are adequately supported by the written description of the application as originally filed, and that the proposed claims are patentable over the prior art. *See* 37 C.F.R. § 42.121; *Idle Free Sys. Inc. v. Bergstrom, Inc.*, Case IPR2012-00027, slip op. at 5–6 (PTAB June 11, 2013) (Paper 26). We address each of these requirements in turn.

1. Reasonable Number of Substitute Claims

A patent owner may propose a reasonable number of substitute claims for each challenged claim. 35 U.S.C. § 316(d)(1). Absent special circumstances, it is presumed that only one substitute claim is needed to replace each challenged claim. 37 C.F.R. § 42.121(a)(3). This presumption may be rebutted by showing that the substitute claims are patentably distinct from each other. *Idle Free*, Paper 26, 8–9. To the extent that no patentable distinction is shown, we may deny entry of the excess claims or group them together for purposes of considering patentability over prior art. *See id.*

In its Motion to Amend, Patent Owner proposes to add claim 21 as a substitute for original claims 1, 3, 4, and 7. Mot. 3. Patent Owner also

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proposes to add “new” substitute claim 30, which depends from claim 21 and is directed to HDO temperatures in the range of 280–305 °C. Mot. 5, 7. Claim 30 is not identified as a substitute for any original claim and, as it depends from claim 21, contains all of the limitations of that claim. Accordingly, claims 21 and 30 are both considered substitutes for original claims 1, 3, 4, and 7. *See Idle Free*, Paper 26, 8. As more than one substitute claim is proposed for a single original claim, for example, both claim 21 and claim 30 substitute for claim 1, Patent Owner must establish a need for new claim 30. *Id.*

Patent Owner argues that claim 30 is needed because its temperature range of 280–305 °C is “narrower and distinct from the 280–330 °C range of proposed substitute claim 21,” further distinguishing the claim from the prior art. Mot. 17; Tr. 66:1–15. Although we agree that the temperature range of 280–305 °C is narrower than 280–330 °C, Patent Owner has not established that this narrower range renders claim 30 *patentably* distinct from claim 21. Mot. 17; Ex. 2019 ¶ 78; Ex. 2041 ¶ 59. We, therefore, are not persuaded that Patent Owner has satisfied its burden to show a need for substitute claim 30. Instead of denying entry of claim 30, however, we exercise our discretion to group claim 30 with claim 21 for purposes of considering patentability of the claims over prior art. *See Idle Free*, Paper 26, 8–9.

2. Written Description Support

Patent Owner bears the burden to show written description support in the original disclosure for each proposed substitute claim. 37 C.F.R. § 42.121(b)(1); 37 C.F.R. § 42.20(c). The test for written description support is “whether the disclosure of the application relied upon reasonably conveys to those skilled in the art that the inventor had possession of the

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claimed subject matter as of the filing date.” *Ariad Pharm., Inc. v. Eli Lilly & Co.*, 598 F.3d 1336, 1351 (Fed. Cir. 2010).

Substitute claim 21 recites obtaining an HDO product having “less than 1 wt-% of high molecular weight hydrocarbons” using “a stream of diluting agent.” Proposed substitute claims 22 and 23, which depend from claim 21, further require the diluting agent be in a ratio of 5–30:1 and 10–30:1, respectively. Thus, claim 21 presumptively encompasses the use of dilution ratios outside a 5–30:1 ratio. *See Liebel-Flarsheim Co. v. Medrad, Inc.*, 358 F.3d 898, 910 (Fed. Cir. 2004) (“[T]he presence of a dependent claim that adds a particular limitation raises a presumption that the limitation in question is not found in the independent claim.”)

Patent Owner argues that obtaining “less than 1 wt-% high molecular weight hydrocarbons” using an unbounded dilution ratio is supported by the reported experimental results and the disclosure that product recycle dilution can prevent or remarkably decrease the reactions between free fatty acids and the formation of high molecular weight compounds during hydrotreating. *See* Mot. 6–7; PO Reply 3; Ex. 2017 ¶ 64.

We are not persuaded by this argument. The reported “surprising[]” experimental results, including the ability to “prevent or remarkably decrease” the formation of high molecular weight hydrocarbons, are directly tied to a dilution ratio of “at least 5:1”:

It was surprisingly observed in examples that product recycle dilution can prevent or remarkably decrease the reactions between free fatty acids and the formation of high molecular weight compounds during hydrotreating, *when at least 5:1 (product recycle):(fresh oil)-ratio was used.*

...

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In the examples it was be (sic) seen that the ratio of *at least* 5:1 (recycle:fresh) significantly decreased the formation of high molecular weight products, when the feedstock contains 10 wt-% of free fatty acids (calculated from fresh oil) is used. Using *at least* 5:1 recycle ratio and reduced reaction temperature, free fatty acids can be processed without the need for deacidification. High quality hydrocarbons are obtained, suitable for the diesel fuel pool with high yield.

Ex. 2017 ¶¶ 64, 73 (emphases added). Moreover, throughout the '094 patent specification, the dilution ratio is described as “5-30:1, preferably 10-30:1, most preferably 12-25:1.” *Id.* ¶¶ 38, 43, 56, 62.

In its reply, Patent Owner points to several paragraphs of the '094 patent disclosure that describe the invention without mentioning a 5-30:1 dilution ratio, and argues that “[t]he examples, which use a 5:1 ratio of product recycle/fresh feed, do not diminish” these “broader statements nor suggest that this is the only ratio possible.” PO Reply 2; Mot. 7; Ex. 2017 ¶¶ 2, 23, 24, 37, 64, 72, 73, 84; Ex. 2041 ¶ 19. We are not persuaded by this argument. First, several of the identified disclosures indicate that the dilution level is “high,” not unbounded.⁶ Ex. 2017 ¶¶ 2, 72. Second, even if other dilution ratios are “possible,” the general descriptions identified by Patent Owner do not establish that these alternate dilution ratios would achieve a product having “less than 1 wt-% of high molecular weight hydrocarbons.” *See* Ex. 2041 ¶ 19; Opp. 5. For example, paragraphs 2, 23, 24, 37, and 72 of the '094 patent specification merely suggest that the level of high molecular weight compounds may be “reduced” or “decreased,” and

⁶ At his deposition, Dr. Klein testified that a “high product recycle/fresh oil ratio” encompasses any dilution ratio. Ex. 1088, 63:22–64:19; Paper 46, 5 (Patent Owner’s Reply to Petitioner’s Motion for Observations). This reading, however, would render the term “high” in the '094 patent specification superfluous.

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not that the specific level of “less than 1 wt-%” may be achieved. *See* Ex. 2017 ¶¶ 2, 23, 24, 37, 72. And paragraphs 64, 73, and 84 of the ’094 patent specification do not support Patent Owner’s argument as they are each directly tied to the use of at least a 5:1 dilution ratio. *Id.* ¶¶ 64, 73, 84.

Patent Owner also asserts that an unbounded dilution ratio is adequately supported because the “same language appeared in original application claim 1.” PO Reply 2. We agree that original application claim 1 discloses using a “stream of diluting agent,” as does proposed claim 21. Original claim 1 does not recite, however, the quality of the resulting product, much less a product having “less than 1 wt-% high molecular weight hydrocarbons.” Ex. 2017, 28 (claim 1). We, therefore, are not persuaded that original claim 1 provides sufficient written description support for proposed claim 21. *See Lizardtech, Inc. v. Earth Resource Mapping, Inc.*, 424 F.3d 1336, 1346 (Fed. Cir. 2005) (noting that, in order to provide adequate written description support for later claims, the original claim must actually support the limitation at issue).

Based on the foregoing, we are not persuaded that Patent Owner has met its burden to show adequate written description support for obtaining a product having “less than 1 wt-% high molecular weight hydrocarbons” using an unbounded dilution ratio, as recited in proposed substitute claim 21 and proposed dependent claims 24–30.

3. *Patentability over the Prior Art*

In the Motion to Amend, Patent Owner combines in substitute claim 21 the limitations from claims 1, 3, 4, and 7, and argues that these limitations now “distinguish the claims over the prior art.” Mot. 17–18. Patent Owner does not address, however, why these claim limitations, either

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in isolation or as combined in substitute claim 21, would render the claim non-obvious. *See* Mot. 18. Nor does Patent Owner meaningfully discuss the knowledge, skill, and creativity of one of ordinary skill in the art with respect to these limitations. *Id.* Accordingly, we are not persuaded that Patent Owner has carried its burden to show that the limitations contained in original claims 1, 3, 4, and 7, either alone or in combination, patentably distinguish claim 21 from the prior art.

We focus, therefore, as have both of the parties, on whether the two newly added limitations—an HDO reaction temperature of 280-330 °C and a hydrodeoxygenated product containing “less than 1 wt-% of high molecular weight hydrocarbons”—render claim 21 patentable over the prior art. *See* Mot. 3, 10–17.

a. *Prior Art (Jakkula)*

Jakkula relates to a process for producing hydrocarbons from biological raw materials that are suitable as diesel fuel. Ex. 1038 ¶¶ 1, 12. Like the '094 patent, Jakkula utilizes a two-step process comprising a HDO step and an isomerization step. In the HDO step, “the structure of the biological component is decomposed, oxygen, nitrogen, phosphorus and sulfur compounds, and light hydrocarbons as gas are removed, and the olefinic bonds are hydrogenated.” *Id.* ¶ 16. In the isomerization step, the product of the HDO step is passed over an isomerization catalyst to initiate branching of the hydrocarbon chains, thereby improving the performance of the product at low temperatures. *Id.*

In Jakkula, the HDO step is performed at temperatures between 200 and 500 °C, and preferably in the range of 300–400 °C. *Id.* ¶ 20. To control the “exothermal character of the reactions” in the HDO step, Jakkula

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discloses that the hydrocarbon reaction products may be recycled back to the reaction chamber as a diluent. *Id.* ¶¶ 19, 24, 61.

In Jakkula, “it was surprisingly found that the problems of the prior art processes may be avoided or at least substantially reduced by the process of the invention having at least two steps.” *Id.* ¶ 16. For example, Jakkula reports that it was surprisingly found “that the use of a biological feed stock in the processes is possible” and that “the composition of the feed may vary considerably without affecting the quality of the end product.” *Id.* ¶ 65. Jakkula further reports that the properties of the resulting product are “excellent” and “very suitable as a component in diesel fuels without any blending restrictions.” *Id.* ¶ 73. Jakkula reports no issues with the formation of high molecular weight hydrocarbons or with plugging within the system. *See id.* ¶¶ 70–73.

b. 280-330 °C

The proposed 280-330 °C temperature range of claim 21 is fully encompassed by Jakkula’s disclosed 200-500 °C range, and partially overlaps the preferred temperature range of 300-400 °C. When a claimed range is encompassed by, or overlaps with, a prior art range, the claimed range is presumed to be obvious. *See In re Peterson*, 315 F.3d 1325, 1329 (Fed. Cir. 2003). “This presumption can be rebutted if it can be shown that the prior art teaches away from the claimed range, or the claimed range produces new and unexpected results.” *Ormco Corp. v. Align Tech., Inc.*, 463 F.3d 1299, 1311 (Fed. Cir. 2006).

Patent Owner argues that the presumption of obviousness is rebutted in this case because a prior art patent to Craig et. al. (U.S. Patent No. 4,992,605, Ex. 1013, “Craig”) allegedly teaches away from the use of HDO

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temperatures below 350 °C. Mot. 11. Craig, which issued in 1995, discloses a series of bench top HDO experiments using various feedstocks. Ex. 1013, 4:3–10, Table 8. Craig reports that at HDO reaction temperatures below 350 °C “the product collection system was plugged with a solid margarine-like material,” and concludes that “350 °C was the lower limit for trouble-free operation.” Ex. 1013, 7:11–13, 9:39–10:16; Ex. 2041 ¶¶ 29–30. Patent Owner asserts that, because Craig, unlike Jakkula, conducted a series of experiments to identify the working temperatures for the HDO step, and because Craig allegedly conducted these experiments using similar feedstocks, pressures, and catalysts as Jakkula, one of ordinary skill in the art would have given Craig’s teachings more weight and would have avoided HDO temperatures below 350 °C. Mot. 11–14; PO Reply 3–4; Ex. 2041 ¶¶ 29–32, 35, 41.

“A reference may be said to teach away when a person of ordinary skill in the art, upon reading a reference, would be discouraged from following the path set out in the reference, or would be led in a direction divergent from the path that was taken by the applicant.” *In re Gurley*, 27 F.3d 551, 553 (Fed. Cir. 1994). “[I]n weighing the suggestive power of each reference, [the Board] must consider the degree to which one reference might accurately discredit another.” *In re Young*, 927 F.2d 588, 591 (Fed. Cir. 1991). When two references do not use directly comparable techniques or operating conditions, the impact of an allegedly discrediting reference may be significantly reduced. *See id.* at 592.

Dr. Sughrue testifies that one of ordinary skill in the art would have understood that the “different reactor configurations and catalysts” used in Jakkula “*could and would* lead to differing optimal temperatures from those reported in

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Craig.” Ex. 1040 ¶ 36 (emphasis added). For example, Dr. Sughrue testifies that one of ordinary skill in the art would have understood that reduced temperatures, as well as dilution—which was used in Jakkula but was not studied as an operating variable in Craig—could “greatly reduce the rate of dimerization and oligomerization of free fatty acids” and would lead to lower levels of high molecular weight hydrocarbons. Ex. 1040 ¶¶ 42, 60, 90; Ex. 1013, 4:11–13. Dr. Sughrue also provides evidence that in the years after the publication of Craig “the activity of hydroprocessing catalysts increased dramatically,” permitting lower reaction temperatures in the HDO step. *Id.* ¶¶ 31, 33. In light of these differences, Dr. Sughrue concludes that one of ordinary skill in the art “would not have been dissuaded from considering HDO reaction temperatures at or near the low end of the preferred temperature range taught in [Jakkula], e.g., 300 °C, or even lower temperatures within the more broadly taught range of 200-500 °C.” Ex. 1040 ¶ 37.

We find Dr. Sughrue’s testimony persuasive. In particular, in light of Jakkula’s disclosed successful results, we are persuaded that one of ordinary skill in the art would not have viewed Craig’s 350 °C minimum temperature for “trouble-free operation” as a line not to be crossed, but would have understood that the optimal and minimum temperatures for the HDO step would vary depending on the particular reactor configuration and operating conditions used. *See In re Boesch*, 617 F.2d 272, 276 (CCPA 1980) (“Discovery of an optimum value of a results effective variable in a known process is ordinarily within the skill in the art.”). Although Dr. Klein presents an opposing view from that of Dr. Sughrue, upon review of both expert declarations and their corresponding depositions, on balance, we find that Dr. Sughrue’s testimony more persuasively considers not only the express teachings of Craig and Jakkula, but also the timing of the two disclosures, the differences in reactor configuration and operating conditions, and

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the knowledge, skill, and reasoning ability of one of ordinary skill in the art.

Syntex (U.S.A.) LLC v. Apotex, Inc., 407 F.3d 1371, 1380 (Fed. Cir. 2005) (“What a reference teaches or suggests must be examined in the context of the knowledge, skill, and reasoning ability of a skilled artisan.”)

We, therefore, are not persuaded that Patent Owner has carried its burden to show that Craig sufficiently teaches away from, or discredits, the lower end of Jakkula’s preferred temperature range to rebut the presumption of obviousness.

c. Less Than 1 wt-% of High Molecular Weight Hydrocarbons

Patent Owner asserts that it would not have been obvious to obtain an HDO product having “less than 1 wt-% of high molecular weight hydrocarbons.” Mot. 15. According to Patent Owner, because one of ordinary skill in the art would not have appreciated “the problem of high molecular weight hydrocarbon formation when hydrodeoxygenating feedstocks containing free fatty acids, no reason existed at the time of the ’094 invention to optimize the prior art HDO processes to minimize the negative effects” of such compounds. *Id.* In support of this argument, Dr. Klein testifies that “[t]o my knowledge no publication before the ’094 patent identified that the presence of free fatty acids in a biological feedstock was a recognized source of problems in hydrodeoxygenation.” Ex. 2019 ¶ 11; Ex. 2041 ¶ 60.

In its Opposition, Petitioner argues that Patent Owner and Dr. Klein “are flat wrong when they claim that no one before the ’094 patent recognized that the processing of streams containing [free fatty acids] could promote the formation of [high molecular weight hydrocarbons]” as the propensity for free fatty acids to form high molecular weight compounds has been “well-known and well-studied in the art for decades,” and was

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expressly acknowledged during prosecution of the '094 patent. Opp. 11–12; Ex. 1040 ¶¶ 39–41.

We find Petitioner's argument persuasive. In particular, during prosecution of the parent application to the '094 patent, the patentee repeatedly asserted that one of ordinary skill in the art would understand that operating an HDO process on biologic feedstocks with high levels of free fatty acids would result in the formation of high molecular weight hydrocarbons. For example, it was argued in a March 17, 2008, Amendment in response to an Office Action that it was known in the art that free fatty acids contributed to the formation of high molecular weight compounds:

As is known in the art, several problems arise during processing of bio-oils and fats, including general deoxygenation activity, potential side reactions, catalyst deactivation due to free fatty acids and high hydrogen consumption in the hydrotreatment step. *Side reactions in the hydrotreatment step, resulting in the formation of heavy molecular weight compounds, are significantly increased, due to the presence of free fatty acids and/or their derivatives in the feed.*

Ex. 1052, 9 (emphasis added). Likewise, in a declaration submitted by Jukka Myllyoja—a common inventor on both the '094 patent and Jakkula—it was asserted that “[a] man skilled in the art would expect to encounter problems when a feed containing high amounts of free fatty acids is hydroprocessed on an industrial scale,” including “[t]he formation of high molecular weight compounds.” Ex. 1048, 3.

In light of the assertions made during prosecution, we are not persuaded that the propensity for free fatty acids to promote the formation of high molecular weight hydrocarbons was unknown prior to the '094 patent. *See also* Ex. 1040 ¶¶ 38–61 (asserting that the

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dimerization of unsaturated free fatty acids was well-known in the art from as early as 1984 and was disclosed in Jakkula (Ex. 1038 ¶ 21)).

Patent Owner further argues that “each part of the claimed process—the low HDO reaction temperature, the dilution, and the low metallic and phosphorus contaminant levels—is needed to achieve” less than 1 wt-% high molecular weight hydrocarbons using feedstock with more than 5 wt-% free fatty acids. Mot. 15. According to Patent Owner, because the synergy of these reaction parameters was not known prior to the ’094 patent, one of skill would not have been able to optimize the Jakkula process to achieve the claimed results. *Id.*; Ex. 2019 ¶ 79; Tr. 31:22–32:6.

Patent Owner identifies Example 5 as alleged support for its argument that all three elements (temperature, dilution, and low levels of impurities) are required to achieve “less than 1 wt-% high molecular weight hydrocarbons.” Mot. 15. Patent Owner does not establish sufficiently, however, that the combination of purified rapeseed oil and stearic acid used in Example 5 was within the purity limitations of proposed substitute claim 21. Ex. 1088, 76:13–24; Ex. 1040 ¶ 73; Ex. 2019 ¶¶ 22, 34, 84. Moreover, Dr. Sughrue testifies that in Figure 5, which represents an experiment run with a feedstock containing high levels of impurities, the level of high molecular weight hydrocarbons was kept below 1 wt-% for at least 8 days. *See* Ex. 1040 ¶ 90. We agree with Dr. Sughrue that “Figure 5 thus illustrates that the combination of a low HDO temperature, dilution, and feeds having low impurities is not necessary to achieve the allegedly surprising result.” *Id.* Accordingly, we are not persuaded that Patent Owner has established that each of the claimed limitations is necessary to achieve an HDO product containing “less than 1 wt-% high molecular weight hydrocarbons,” or that

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one of ordinary skill in the art could not optimize reaction conditions to minimize the level of “high molecular weight hydrocarbons” without the disclosure of the ’094 patent.

Based on the foregoing, Patent Owner has not met its burden to demonstrate that claim 21 is patentable. As claim 30 is grouped with claim 21 for purposes of analyzing the patentability of the claims over the prior art, we are also not persuaded that claim 30 is patentable. Moreover, even if we were to address claim 30 individually, Patent Owner has not demonstrated that this claim is patentable, as Patent Owner relies upon essentially the same teaching away argument for claim 30 that we rejected for claim 21.

d. *Proposed Substitute Claims 22–30*

Patent Owner also argues that it would not have been obvious from the combined teachings of Jakkula and Harrison to obtain the dilution ratios of substitute claims 22 and 23:

Although Harrison uses dilution to control the temperature of hydrogenation reactions (Ex. 1014 at 10:66-11:2), it provides no reason to adjust the dilution ratio in combination with a low reaction temperature and low metallic and phosphorus contaminant levels to achieve less than 1 wt-% high molecular weight hydrocarbons in an HDO reaction, as claimed.

Mot. 16.

Patent Owner’s argument, however, is limited to the grounds of unpatentability asserted by Petitioner, and does not address the “prior art known to the patent owner.” *See Idle Free*, Paper 26, 7. Patent Owner also does not address the patentability of claims 22 and 23 with respect to the knowledge and skill of an ordinary artisan. As noted above, the propensity for free fatty acids to form high molecular weight hydrocarbons was known. Dr. Sughrue testifies that, because these reactions are generally second

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order, one of ordinary skill in the art would have understood that dilution should significantly reduce the formation of these high molecular weight hydrocarbons. Ex. 1040 ¶¶ 41–42, 51, 88; Opp. 12. Dr. Sughrue further testifies that one of ordinary skill in the art would be able to determine the optimal dilution ratio while working within the dilution ratios set forth in the prior art. Ex. 1040 ¶¶ 39–42, 90, 93; Ex. 1014, 14:22–39 (disclosing dilution ratios between 1:3 to 1:99); Ex. 1008, 2 (disclosing dilution ratios between 5:1 to 200:1). In light of this testimony, and Patent Owner’s failure to specifically address the knowledge and skill of an ordinary artisan in the Motion to Amend, we are not persuaded that Patent Owner has established that claims 22 and 23 are patentable.

Patent Owner does not individually address the patentability of claims 24–29, relying instead on its arguments with respect to substitute claim 21. As Patent Owner has not carried its burden to show that claim 21 is patentable, we are not persuaded that Patent Owner has carried its burden to show that claims 24–29 are patentable.

For all the foregoing reasons,⁷ Patent Owner has not, in its Motion to Amend, demonstrated the patentability of proposed substitute claims 21–30 to the ’094 patent.

III. CONCLUSION

Patent Owner has not demonstrated by a preponderance of the evidence that proposed substitute claims 21–30 are patentable. Therefore,

⁷ Petitioner also argues that claims 21–30 are indefinite. Opp. 2–3. In light of our determination that Petitioner has not shown by a preponderance of the evidence that claims 21–30 satisfy the written description and other requirements for patentability, we decline to address Petitioner’s indefiniteness argument.

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we deny the Motion to Amend with respect to the substitution of claims 21–30. We grant the Motion to Amend solely with respect to Patent Owner’s non-contingent request to cancel claims 1–20.

IV. ORDER

In consideration of the foregoing, it is

ORDERED that Patent Owner’s Motion to Amend is *granted* with respect to the cancelation of claims 1–20;

FURTHER ORDERED that Patent Owner’s Motion to Amend is otherwise *denied*; and

FURTHER ORDERED that because this is a final decision, parties to the proceeding seeking judicial review of the decision must comply with the notice and service requirements of 37 C.F.R. § 90.2.

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(12) **United States Patent**
Myllyoja et al.

(10) **Patent No.:** **US 8,212,094 B2**

(45) **Date of Patent:** ***Jul. 3, 2012**

(54) **PROCESS FOR THE MANUFACTURE OF
DIESEL RANGE HYDROCARBONS**

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(75) Inventors: **Jukka Myllyoja**, Vantaa (FI); **Pekka Aalto**, Porvoo (FI); **Pekka Savolainen**, Vantaa (FI); **Veli-Matti Purola**, Hamari (FI); **Ville Alopaeus**, Espoo (FI); **Johan Grönqvist**, Tolkkinen (FI)

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(73) Assignee: **Neste Oil Oyj**, Espoo (FI)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

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(65) **Prior Publication Data**

US 2011/0282116 A1 Nov. 17, 2011

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Related U.S. Application Data

(62) Division of application No. 11/477,922, filed on Jun. 30, 2006, now Pat. No. 8,022,258.

(60) Provisional application No. 60/695,853, filed on Jul. 5, 2005.

(51) **Int. Cl.**
C07C 1/00 (2006.01)

(52) **U.S. Cl.** **585/240**; 585/241

(58) **Field of Classification Search** None
See application file for complete search history.

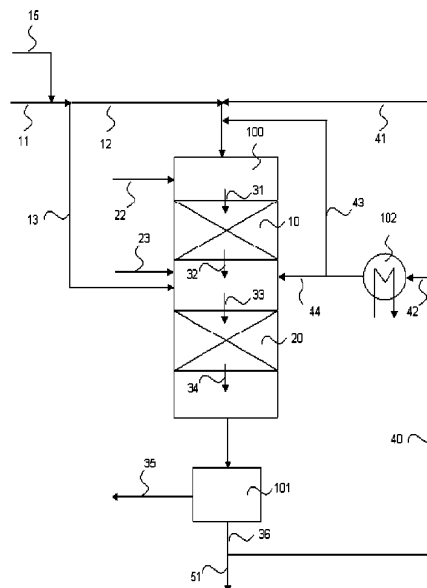
Primary Examiner — Yate K Cutliff

(74) *Attorney, Agent, or Firm* — Birch, Stewart, Kolasch & Birch, LLP

(57) **ABSTRACT**

The invention relates to a process for the manufacture of diesel range hydrocarbons wherein a feed is hydrotreated in a hydrotreating step and isomerized in an isomerization step, and a feed comprising fresh feed containing more than 5 wt % of free fatty acids and at least one diluting agent is hydrotreated at a reaction temperature of 200-400° C., in a hydrotreating reactor in the presence of catalyst, and the ratio of the diluting agent/fresh feed is 5-30:1.

20 Claims, 5 Drawing Sheets



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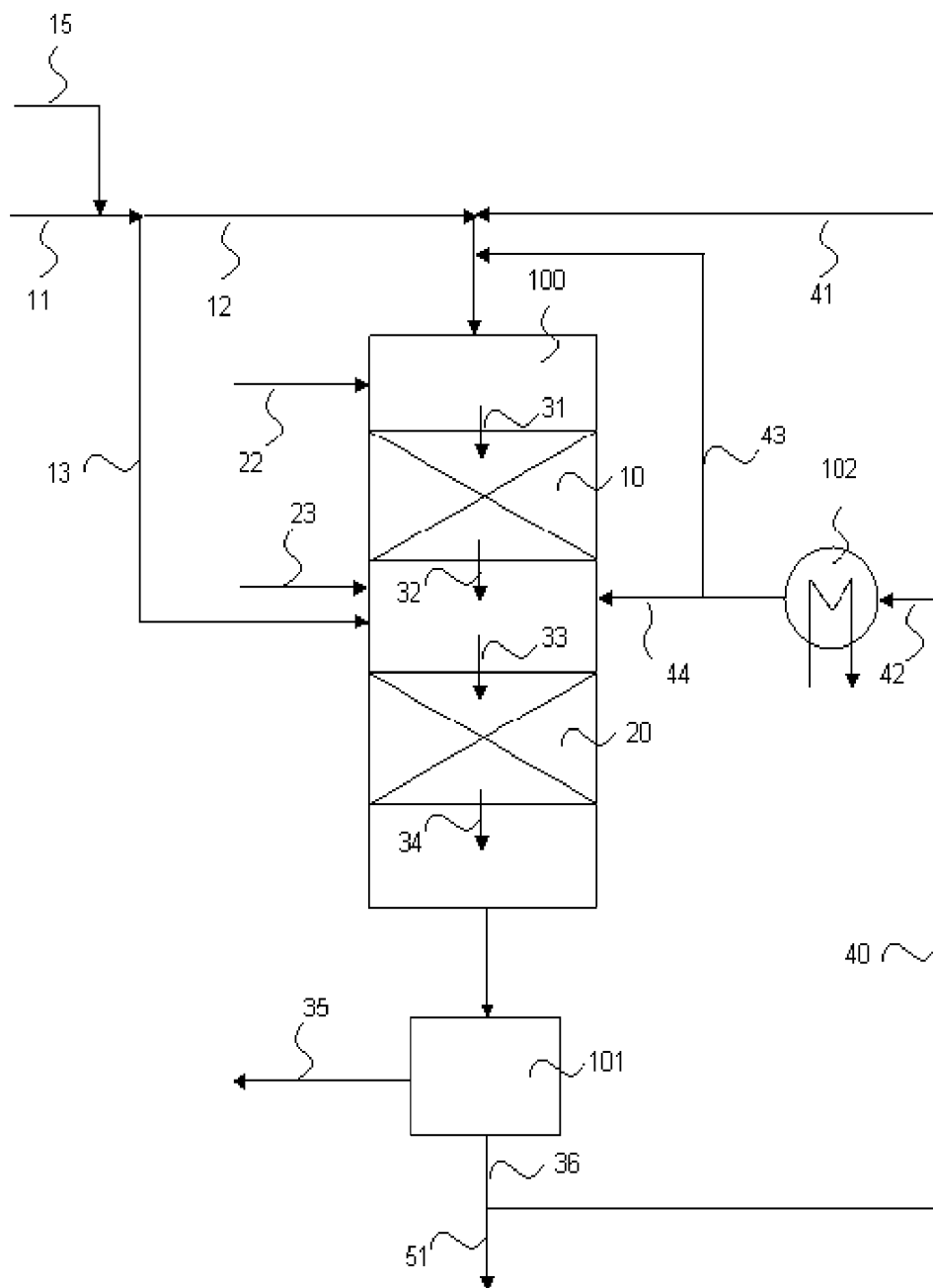


Fig. 1

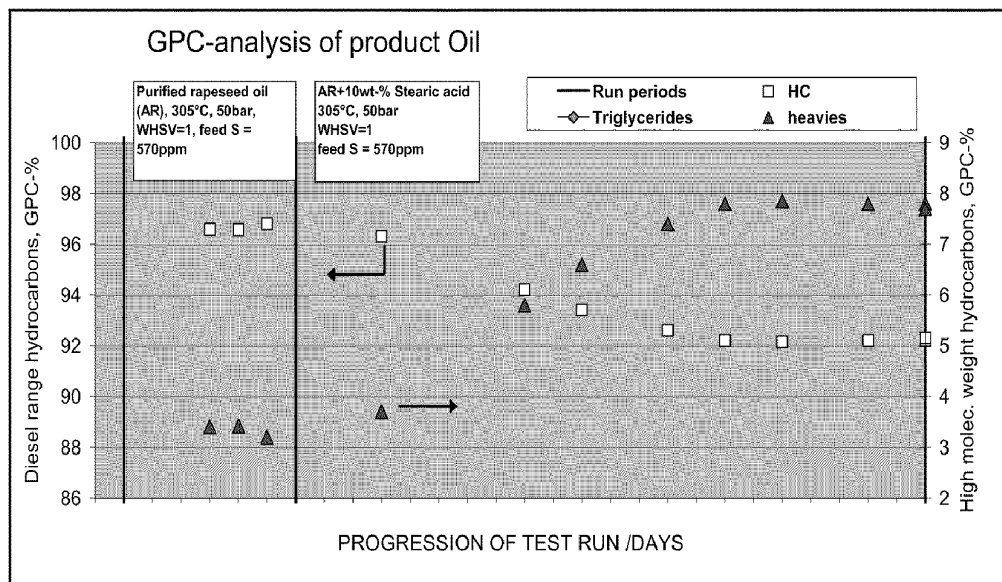


Fig. 2

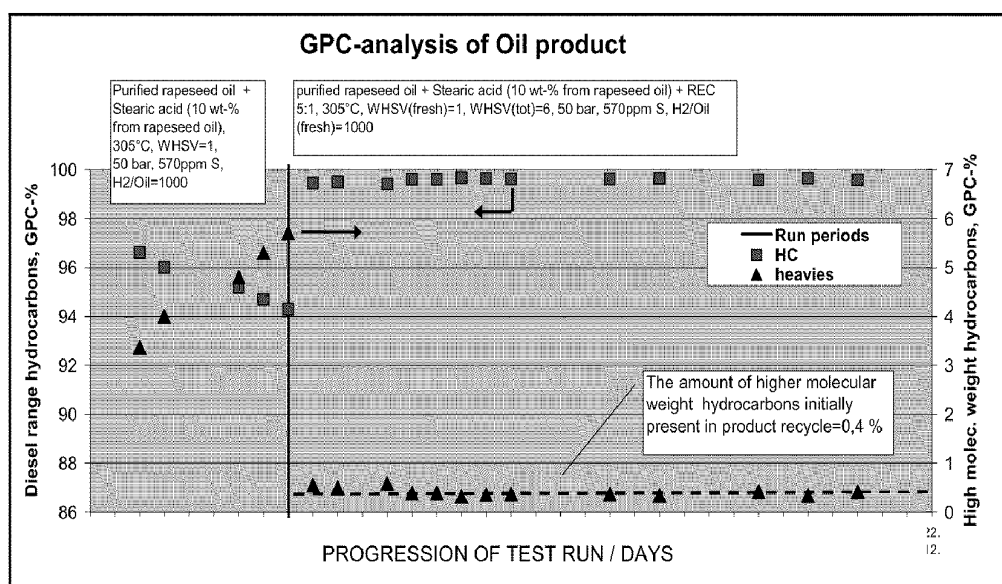


Fig. 3

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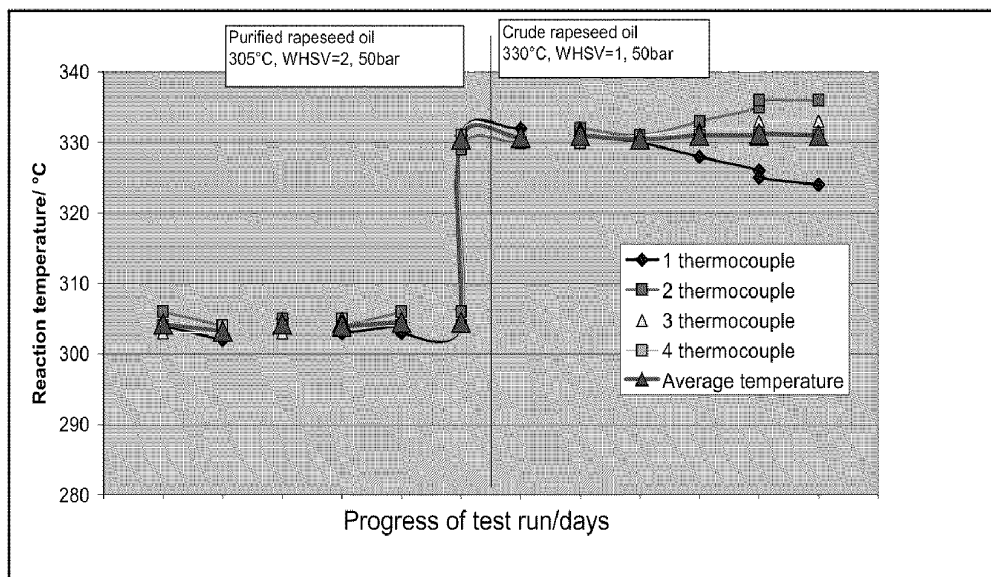


Fig. 4

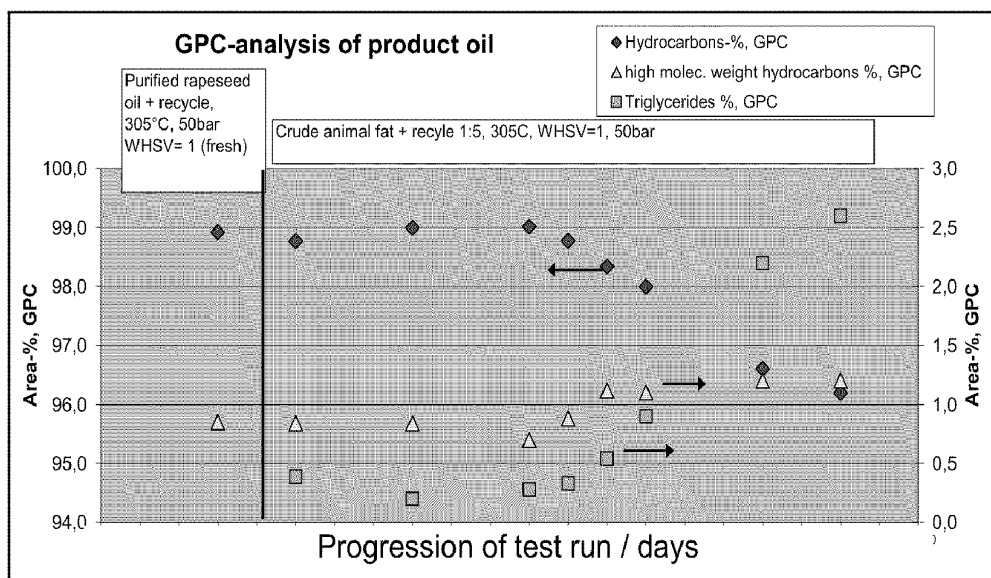


Fig. 5

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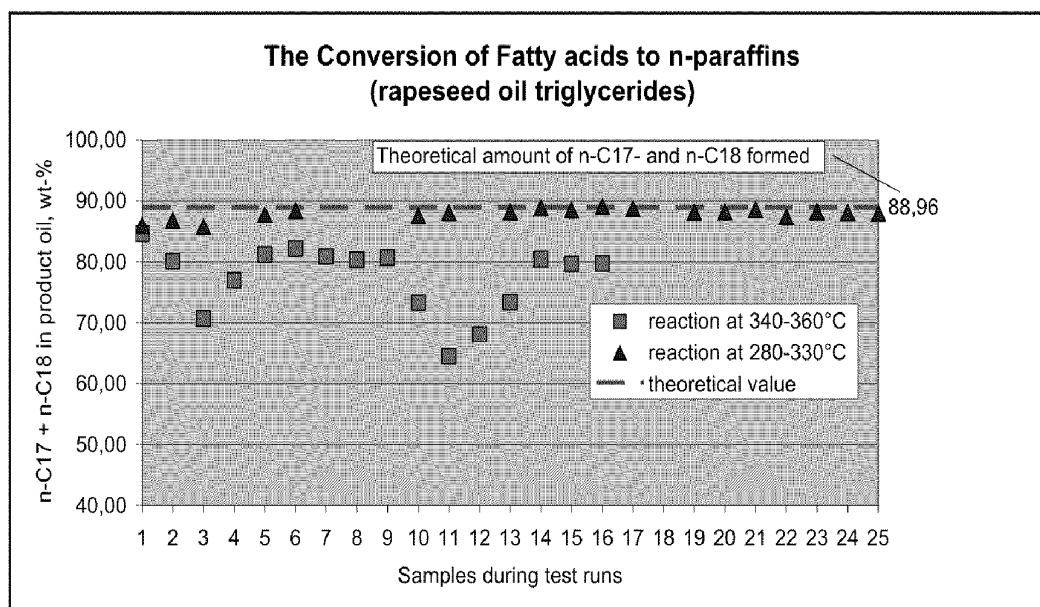


Fig. 6

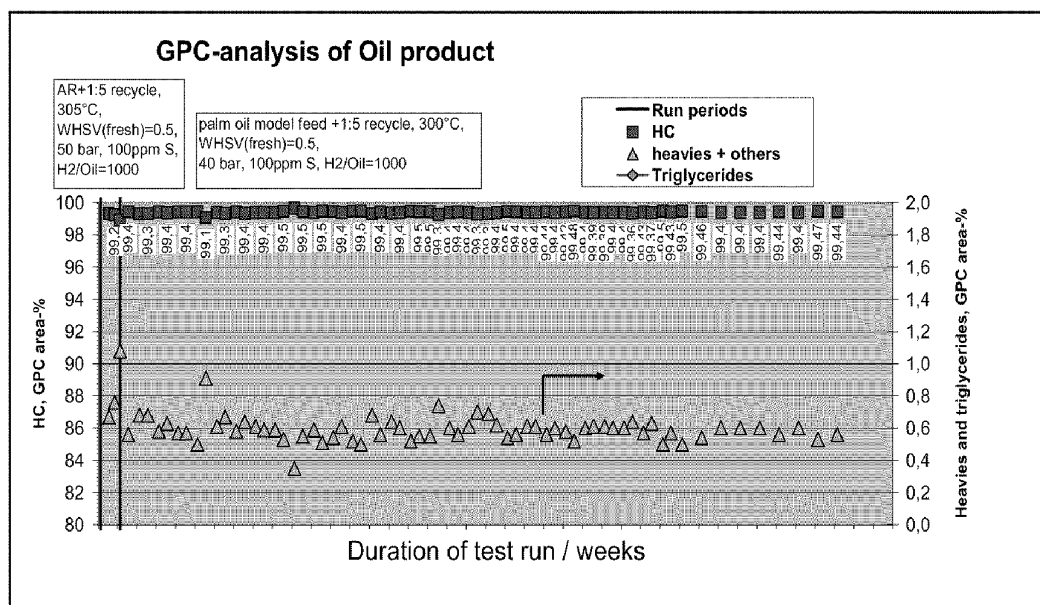


Fig. 7

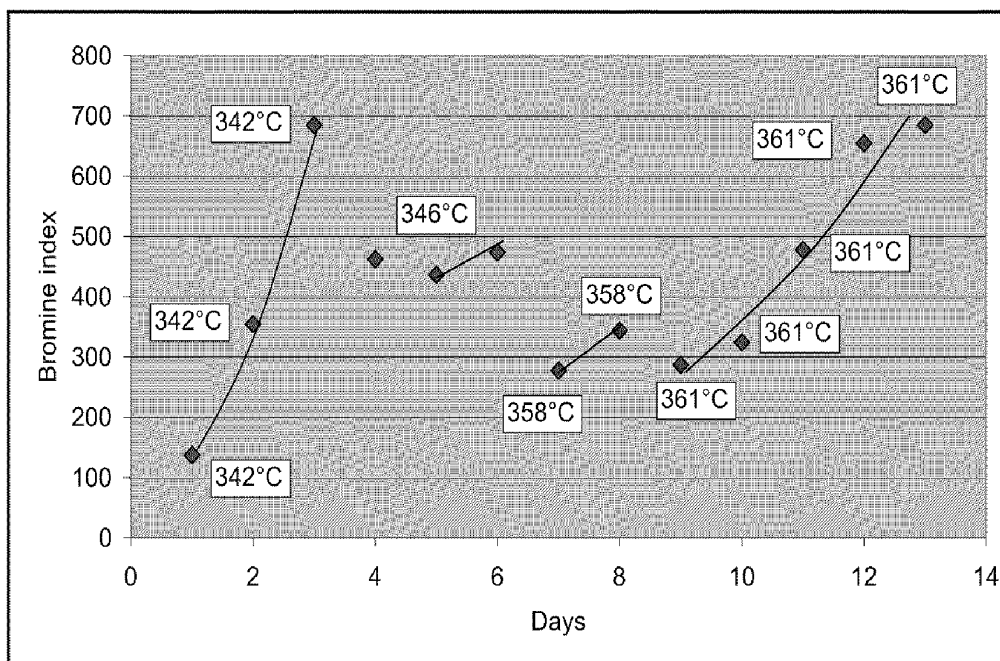


Fig 8

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**PROCESS FOR THE MANUFACTURE OF
DIESEL RANGE HYDROCARBONS****CROSS REFERENCE TO RELATED
APPLICATIONS**

This application is a Divisional of application Ser. No. 11/477,922 filed on Jun. 30, 2006 now U.S. Pat. No. 8,022, 258, which claims the benefit of U.S. Provisional Application No. 60/695,853 filed on Jul. 5, 2005. The entire contents of all of the above applications is hereby incorporated by reference.

FIELD OF THE INVENTION

The invention relates to an improved process for the manufacture of hydrocarbons, particularly diesel range hydrocarbons from bio oils and fats, wherein the formation of higher molecular weight compounds is reduced. The invention also relates to processing of feedstock containing free fatty acids, using a high product recycle/fresh oil-ratio at reduced reaction temperatures.

BACKGROUND OF THE INVENTION

Environmental interests and an increasing demand for diesel fuel, especially in Europe, encourage fuel producers to employ more intensively available renewable sources. In the manufacture of diesel fuels based on biological raw materials, the main interest has concentrated on vegetable oils and animal fats comprising triglycerides of fatty acids. Long, straight and mostly saturated hydrocarbon chains of fatty acids correspond chemically to the hydrocarbons present in diesel fuels. However, neat vegetable oils display inferior properties, particularly extreme viscosity and poor stability and therefore their use in transportation fuels is limited.

Conventional approaches for converting vegetable oils or other fatty acid derivatives into liquid fuels comprise transesterification, catalytic hydrotreatment, hydrocracking, catalytic cracking without hydrogen and thermal cracking among others. Typically triglycerides, forming the main component in vegetable oils, are converted into the corresponding esters by the transesterification reaction with an alcohol in the presence of catalysts. The obtained product is fatty acid alkyl ester, most commonly fatty acid methyl ester (FAME). Poor low-temperature properties of FAME however limit its wider use in regions with colder climatic conditions.

Said properties are the result of the straight chain nature of the FAME molecule and thus double bonds are needed in order to create even bearable cold flow properties. Carbon-carbon double bonds and ester groups however decrease the stability of fatty acid esters, which is a major disadvantage of transesterification technology. Further, Schmidt, K., Gerpen J. V.: SAE paper 961086 teaches that the presence of oxygen in esters results in undesirable higher emissions of NO_x , in comparison to conventional diesel fuels.

Undesired oxygen may be removed from fatty acids or their esters by deoxygenation reactions. The deoxygenation of bio oils and fats, which are oils and fats based on biological material, to produce hydrocarbons suitable as diesel fuel products, may be carried out by catalytic hydroprocessing, such as hydrocracking, but also more controlled hydrotreating conditions may be utilized.

During hydrotreating, particularly hydrodeoxygenation oxygen containing groups are reacted with hydrogen and removed through formation of water and therefore this reaction requires rather high amounts of hydrogen. Due to the highly exothermic nature of these reactions, the control of

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reaction heat is extremely important. Impure plant oil/fat or animal fat/oil, high reaction temperatures, insufficient control of reaction temperature or low hydrogen availability in the feed stream may cause unwanted side reactions, such as cracking, polymerisation, ketonisation, cyclisation and aromatisation, and coking of the catalyst. These side reactions also decrease the yield and the properties of diesel fraction obtained.

Unsaturated feeds and free fatty acids in bio oils and fats may also promote the formation of heavy molecular weight compounds, which may cause plugging of the preheating section and decrease catalyst activity and life.

The fatty acid composition, size and saturation degree of the fatty acid may vary considerably in feedstock of different origin. The melting point of bio oil or fat is mainly a consequence of saturation degree. Fats are more saturated than liquid oils and in this respect need less hydrogen for hydrogenation of double bonds. Double bonds in a fatty acid chain also promote different kinds of side reactions, such as oligomerisation/polymerization, cyclisation/aromatisation and cracking reactions, which deactivate catalyst, increase hydrogen consumption and reduce diesel yield.

Plant oils/fats and animal oils/fat may contain typically 0-30% of free fatty acids, which are formed during enzymatic hydrolysis of triglycerides especially when oil seeds are kept in humid atmosphere. Free fatty acids can be also formed during purification of bio oils and fats, especially during caustic wash i.e. alkali catalyzed hydrolysis. The amount of free fatty acids present in plant/vegetable oils is typically 1-5 wt % and in animal fat 10-25 wt-%. Free fatty acids are corrosive in their nature, they can attack against materials of unit or catalyst and can promote some side reactions. Free fatty acids react very efficiently with metal impurities producing metal carboxylates, which promote side reaction chemistry.

Fatty acids may also promote the formation of heavy compounds. The boiling range of these heavy compounds is different from the range of diesel fuel and may shorten the life of isomerisation catalyst. Due to the free fatty acids contained in bio oils and fats, the formation of heavy molecular weight compounds are significantly increased compared to triglyceridic bio feeds, which have only low amount of free fatty acids (<1%).

Biological raw materials often contain metal compounds, organic nitrogen, sulphur and phosphorus compounds, which are known catalyst inhibitors and poisons inevitably reducing the service life of the catalyst and necessitating more frequent catalyst regeneration or change. Metals in bio oils/fats inevitably build up on catalyst surface and change the activity and selectivity of the catalyst. Metals can promote some side reactions, but blocking of catalyst active sites typically decreases the activity and thus metal impurities such as Na, Ca, and Mg compounds should be removed as efficiently as possible.

Hydrolysis of triglycerides produces also diglycerides and monoglycerides, which are partially hydrolyzed products. Diglycerides and monoglycerides are surface-active compounds, which can form emulsions and make liquid/liquid separations of water and oil more difficult. Bio oils and fats can also contain other glyceride-like surface-active impurities like phospholipids (for example lecithin), which have phosphorus in their structures. Phospholipids are gum like materials, which can be harmful for catalysts. Natural oils and fats also contain other types of components, such as waxes, sterols, tocopherols and carotenoids, some metals and organic sulphur compounds as well as organic nitrogen com-

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pounds. These compounds can be harmful for catalysts or pose other problems in processing.

U.S. Pat. Nos. 4,992,605 and 5,705,722 describe processes for the production of diesel fuel additives by conversion of bio oils into saturated hydrocarbons under hydroprocessing conditions with CoMo and NiMo catalysts. The process operates at high temperatures of 350-450° C. and produces n-paraffins and other hydrocarbons. The product has a high cetane number but poor cold properties (melting point >20° C.), which limits the amount of product that can be blended in conventional diesel fuels in summer time and prevent its use during winter time. The formation of heavy compounds with a boiling point above 343° C. was observed, especially when a fatty acid fraction was used as a feed. A reaction temperature with a lower limit of 350° C. was concluded as a requirement for trouble-free operation.

A two-step process is disclosed in FI 100248, for producing middle distillates from vegetable oil by hydrogenating fatty acids or triglycerides of vegetable oil origin using commercial sulphur removal catalysts, such as NiMo and CoMo, to give n-paraffins, followed by isomerising said n-paraffins using metal containing molecular sieves or zeolites to obtain branched-chain paraffins. The hydrotreating was carried out at rather high reaction temperatures of 330-450° C., preferably 390° C. Hydrogenating fatty acids at those high temperatures leads to shortened catalyst life resulting from coking and formation of side products.

EP 1 396 531 describes a process containing at least two steps, the first one being a hydrodeoxygenation step and the second one being a hydroisomerisation step utilizing counter-current flow principle, and using biological raw material containing fatty acids and/or fatty acid esters as the feedstock. The process comprises an optional stripping step.

Deoxygenation of plant oils/fats and animal fats with hydrogen use a large amount of hydrogen and at the same time releases significant amount of heat. Heat is produced from deoxygenation reactions and from double bond hydrogenation. Different feedstocks produce significantly different amounts of reaction heat. The variation of reaction heat produced is mainly dependent on double bond hydrogenation. The average amount of double bonds per triglyceride molecule can vary from about 1.5 to more than 5 depending on the source of bio oil or fat.

FR 2,607,803 describes a process for hydrocracking of vegetable oils or their fatty acid derivatives under pressure to give hydrocarbons and to some extent acid. The catalyst contains a metal dispersed on a support. A high temperature of 370° C. did not result complete oxygen removal or high selectivity of n-paraffins. The product mixture formed, contained also some intermediate fatty acid compounds.

Formation of water during hydrotreatment results from the deoxygenation of triglyceride oxygen by the means of hydrogen (hydrodeoxygenation). Deoxygenation under hydrodeoxygenation conditions is to some extent accompanied by a decarboxylation reaction pathway and a decarbonylation reaction pathway. Deoxygenation of fatty acid derivatives by decarboxylation and/or decarbonylation reactions forms carbon oxides (CO₂ and CO) and aliphatic hydrocarbon chains with one carbon atom less than in the original fatty acid molecule. Decarb-reactions mean here decarboxylation and/or decarbonylation reactions.

The feasibility of decarboxylation varies greatly with the type of carboxylic acid or derivative thereof used as the starting material. Alpha-hydroxy, alpha-carbonyl and dicarboxylic acids are activated forms and thus they are more easily deoxygenated by decarb-reactions. Saturated aliphatic acids

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are not activated this way and generally are difficult to deoxygenate through decarb-reactions.

Decarboxylation of carboxylic acids to hydrocarbons by contacting carboxylic acids with heterogeneous catalysts was suggested by Maier, W. F. et al: *Chemische Berichte* (1982), 115 (2), 808-12. Maier et al tested Ni/Al₂O₃ and Pd/SiO₂ catalysts for decarboxylation of several carboxylic acids. During the reaction the vapors of the reactant were passed through a catalytic bed together with hydrogen. Hexane represented the main product of the decarboxylation of the tested compound heptanoic acid. When nitrogen was used instead of hydrogen no decarboxylation was observed.

U.S. Pat. No. 4,554,397 discloses a process for the manufacture of linear olefins from saturated fatty acids or esters, suggesting a catalytic system consisting of nickel and at least one metal selected from the group consisting of lead, tin and germanium. With other catalysts, such as Pd/C, low catalytic activity and cracking to saturated hydrocarbons, or formation of ketones when Raney-Ni was used, were observed.

OBJECT OF THE INVENTION

An object of the invention is an improved process for the manufacture of diesel range hydrocarbons from bio oils and fats, with high selectivity, essentially without side reactions and with high diesel yield.

A further object of the invention is an improved process for the manufacture of diesel range hydrocarbons from bio oils and fats, wherein the extent of high molecular weight compounds formed during hydrotreating is decreased and the stability of the catalyst is increased.

A still further object of the invention is an improved process for the manufacture of diesel range hydrocarbons from bio oils and fats, wherein the hydrotreatment of triglyceride feedstock containing free fatty acids is carried out using dilution of fresh feed and reduced reaction temperature.

A still further object of the invention is an improved process for the manufacture of diesel range hydrocarbons from bio oils and fats, which process produces high quality diesel component with high yield.

Characteristic features of the process according to the invention are provided in the claims.

DEFINITIONS

Here hydroprocessing is understood as catalytic processing of organic material by all means of molecular hydrogen.

Here hydrotreatment is understood as a catalytic process, which removes oxygen from organic oxygen compounds as water (hydrodeoxygenation, HDO), sulphur from organic sulphur compounds as dihydrogen sulphide (H₂S) (hydrodesulphurisation, HDS), nitrogen from organic nitrogen compounds as ammonia (NH₃) (hydrodenitrogenation, HDN) and halogens, for example chlorine from organic chloride compounds as hydrochloric acid (HCl) (hydrodechlorination, HDCl), typically under the influence of sulphided NiMo or sulphided CoMo catalysts.

Here deoxygenation is understood to mean removal of oxygen from organic molecules, such as fatty acid derivatives, alcohols, ketones, aldehydes or ethers by any means previously described.

Here hydrodeoxygenation (HDO) of triglycerides or other fatty acid derivatives or fatty acids is understood to mean the removal of carboxyl oxygen as water by the means of molecular hydrogen under the influence of catalyst.

Here decarboxylation and/or decarbonylation of triglycerides or other fatty acid derivatives or fatty acids is understood

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to mean removal of carboxyl oxygen as CO₂ (decarboxylation) or as CO (decarbonylation) with or without the influence of molecular hydrogen. Decarboxylation and decarbonylation reactions either together or alone are referred to as decarb-reactions.

Here hydrocracking is understood as catalytic decomposition of organic hydrocarbon materials using molecular hydrogen at high pressures.

Here hydrogenation means saturation of carbon-carbon double bonds by means of molecular hydrogen under the influence of a catalyst.

Here n-paraffins mean normal alkanes or linear alkanes that do not contain side chains.

Here isoparaffins mean alkanes having one or more C₁-C₉, typically C₁-C₂ alkyl side chains, typically mono-, di-, tri- or tetramethylalkanes.

The feed (total feed) to the hydrotreating unit is here understood to comprise fresh feed and at least one dilution agent.

SUMMARY OF THE INVENTION

The present invention relates to an improved process for the manufacture of hydrocarbons from renewable sources, such as plant oils/fats and animal oils/fats, comprising a hydrotreating step and an isomerisation step. Particularly the invention relates to the transformation of the starting materials comprising triglycerides, fatty acids and derivatives of fatty acids or combinations of thereof, into n-paraffins with reduced formation of high molecular weight hydrocarbons using dilution of fresh feed and reduced reaction temperature in the hydrotreating step and converting the obtained n-paraffins into diesel range branched alkanes using isomerisation, with high diesel yield. The hydrotreating step is carried out contacting the feed comprising fresh feed and at least one diluting agent with a hydrotreatment catalyst under hydrotreatment conditions. Then the obtained product is isomerised with an isomerisation catalyst under isomerisation conditions. The hydrocarbon oil formed via this process is a high quality diesel component.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 schematically shows the operation of the hydrotreatment process.

FIG. 2 shows the increase of formation of high molecular weight hydrocarbons when 10 wt-% free fatty acids was fed along with purified rapeseed oil triglycerides without product recycle.

FIG. 3 shows the effect of product recycle on preventing the formation of unwanted higher molecular weight by-product.

FIG. 4 shows reaction temperature profile over catalyst bed and performance of crude rapeseed oil.

FIG. 5 shows performance of crude animal fat.

FIG. 6 shows the conversion of rapeseed oil triglycerides to n-paraffins.

FIG. 7 shows the stability of catalyst as stabile operation was maintained and the formation of heavies was steady over the whole test run of over 9 months.

FIG. 8 shows that the bromine indexes increased during run even if temperature compensation of catalyst was used.

DETAILED DESCRIPTION OF THE INVENTION

It was surprisingly found that dilution of fresh feed in the hydrotreatment step, in combination with decreased reaction temperature reduces the undesired side reactions and

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improves reaction selectivity, particularly when a starting material containing free fatty acids is used. The diluting agent can be a hydrocarbon of biological origin and/or non-biological origin. The dilution agent can also be recycled product from the process (product recycle). The diluting agent/fresh feed-ratio is 5-30:1, preferably 10-30:1 and most preferably 12-25:1.

A preferable embodiment of the invention and of the hydrotreatment step is illustrated in FIG. 1, wherein a hydrotreatment process configuration is provided, comprising one or more catalyst beds in series, hydrotreated product recycle introduction on the top of the first catalyst bed and fresh feed, quench liquid and hydrogen introduction on top of each catalyst beds. This results in improved control of the reaction temperature in the catalyst beds and hence diminishes undesired side reactions.

In FIG. 1 the hydrotreatment reactor 100 comprises two catalyst beds 10 and 20. Fresh feed 11 is introduced as streams 12 and 13 on the catalyst beds 10 and 20, respectively, and hydrogen as stream 22 and 23 on the catalyst beds 10 and 20, respectively. The fresh feed stream 12 is first mixed with the hydrotreated product recycle stream 41 and quench liquid stream 43 and the resulting mixture 31, diluted in the fresh feed concentration, is then introduced on the catalyst bed 10. In order to obtain a required sulphur concentration in the feed stream 31, required amount of sulphur make up is added to the fresh feed stream 11 via stream 15. As mixture 31 passes through the catalyst bed 10 with the hydrogen stream 22, fatty acids and fatty acid derivatives of the fresh feed stream 12 are converted to the corresponding reaction products. A two-phase stream 32 is withdrawn from the bottom of the catalyst bed 10 and is mixed with the fresh feed stream 13, quench liquid stream 44 and the hydrogen stream 23. The formed vapor-liquid mixture 33, diluted in the fresh feed concentration, is then introduced on the catalyst bed 20 at reduced temperature due to cooling effect of the hydrogen, quench liquid and fresh feed, passed through the catalyst bed 20 and finally withdrawn from the catalyst bed as a product stream 34. The stream 34 is separated in to a vapor stream 35 and liquid stream 36 in the high temperature separator 101. Vapor stream 35 is rich in hydrogen and is directed to further treatment. Part of the liquid stream 36 is returned to the reactor 100 as recycle stream 40, which is further divided to dilution stream 41 and total quench liquid stream 42. The quench liquid stream 42 is cooled in the heat exchanger 102 to provide adequate cooling effect on the top of the catalyst beds 10 and 20. Hydrotreated product stream 51 is directed from the hydrotreatment step to further processing.

The catalyst beds 10 and 20 may be located in the same pressure vessel or in separate pressure vessels. In the embodiment where the catalyst beds are in the same pressure vessels the hydrogen streams 22 and 23 may alternatively be introduced on the catalyst bed 10 and then be passed through the catalyst beds 10 and 20. In the embodiment where the catalyst beds are in separate pressure vessels, the catalyst beds may operate in parallel mode with separate dilution streams, hydrogen streams and quench liquid streams. The number of catalyst beds may be one or two or more than two.

The sulphur make up to the hydrotreatment step may be introduced with the fresh feed stream 11. Alternatively, required amount of sulphur may be fed with the hydrogen streams 22 and 23 as gaseous sulphur compound such as hydrogen sulphide.

Hydrogen is fed to the hydrotreating reactor in excess of the theoretical hydrogen consumption. During the hydrotreating step, triglyceride oils, fatty acids and derivatives thereof are almost theoretically converted to n-paraffins

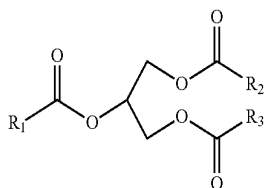
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without or almost without side reactions. Additionally, propane is formed from the glycerol part of the triglycerides, water and CO and/or CO₂ from carboxylic oxygen, H₂S from organic sulphur compounds and NH₃ from organic nitrogen compounds. Using the above described procedures in the hydrotreating step, the temperature needed for reactions to start up is achieved in the beginning of each catalyst bed, the temperature increase in the catalyst beds is limited, harmful and partially converted product intermediates can be avoided and the catalyst life is extended considerably. The temperature at the end of the catalyst bed is controlled by net heat of reactions and to the extent of the dilution agent used. The dilution agent may be any hydrocarbon available, of biological origin or non-biological origin. It can also be recycled product from the process. Fresh feed content from feed (total feed) is be less than 20 wt-%. If the product recycle is used, product recycle/fresh feed ratio is 5-30:1, preferably 10-30:1, most preferably 12-25:1. After the hydrotreatment step, the product is subjected to an isomerization step.

Feedstock

The bio oil and/or fat used as the fresh feed in the process of the present invention originates from renewable sources, such as fats and oils from plants and/or animals and/or fish and compounds derived from them. The basic structural unit of a typical plant or vegetable or animal oil/fat useful as the feedstock is a triglyceride, which is a triester of glycerol with three fatty acid molecules, having the structure presented in the following formula I:



Structure of triglyceride

In formula I R₁, R₂ and R₃ are alkyl chains. Fatty acids found in natural triglycerides are almost solely fatty acids of even carbon number. Therefore R₁, R₂, and R₃ typically are C₅-C₂₃ alkyl groups, mainly C₁₁-C₁₉ alkyl groups and most typically C₁₅ or C₁₇ alkyl groups. R₁, R₂, and R₃ may contain carbon-carbon double bonds. These alkyl chains can be saturated, unsaturated or polyunsaturated.

Suitable bio oils are plant and vegetable oils and fats, animal fats, fish oils, and mixtures thereof containing fatty acids and/or fatty acid esters. Examples of suitable materials are wood-based and other plant-based and vegetable-based fats and oils such as rapeseed oil, colza oil, canola oil, tall oil, sunflower oil, soybean oil, hempseed oil, olive oil, linseed oil, mustard oil, palm oil, peanut oil, castor oil, coconut oil, as well as fats contained in plants bred by means of gene manipulation, animal-based fats such as lard, tallow, train oil, and fats contained in milk, as well as recycled fats of the food industry and mixtures of the above. Bio oil and fat suitable as fresh feed may comprise C₁₂-C₂₄ fatty acids, derivatives thereof such as anhydrides or esters of fatty acids as well as triglycerides of fatty acids or combinations of thereof. Fatty acids or fatty acid derivatives, such as esters may be produced via hydrolysis of bio oils or by their fractionalization or transesterification reactions of triglycerides.

In order to avoid catalyst deactivation and undesired side reactions the feed shall comply with the following require-

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ments: The amount of alkaline and alkaline earth metals, calculated as elemental alkaline and alkaline earth metals, in the feed is below 10, preferably below 5 and most preferably below 1 w-ppm. The amount of other metals, calculated as elemental metals, in the feed is below 10, preferably below 5 and most preferably below 1 w-ppm. The amount of phosphorus, calculated as elemental phosphorus is below 30, preferably below 15 and most preferably below 5 w-ppm.

In many cases the feedstock, such as crude plant oil or animal fat, is not suitable as such in processing because of high impurity content and thus the feedstock is preferably purified using suitably one or more conventional purification procedures before introducing it to the hydrotreating step of the process. Examples of some conventional procedures are provided below:

Degumming of plant oils/fats and animal oils/fats means the removal of phosphorus compounds, such as phospholipids. Solvent extracted vegetable oils often contain significant amounts of gums, typically 0.5-3% by weight, which are mostly phosphatides (phospholipids) and therefore a degumming stage is needed for crude plant oils and animal fats in order to remove phospholipids and metals present in crude oils and fats. Iron and also other metals may be present in the form of metal-phosphatide complexes. Even a trace amount of iron is capable of catalysing oxidation of the oil or fat.

Degumming is performed by washing the feed at 90-105° C., 300-500 kPa(a), with H₃PO₄, NaOH and soft water and separating the formed gums. A major amount of metal components, which are harmful for the hydrotreatment catalyst, are also removed from the feedstock during the degumming stage. The moisture content of the degummed oil is reduced in dryer at 90-105° C., 5-50 kPa(a).

A feedstock, which is optionally degummed or refined in another conventional way, may be bleached. In the bleaching the degummed or refined feedstock is heated and mixed with natural or acid-activated bleaching clay. Bleaching removes various impurity traces left from other pretreatment steps like degumming, such as chlorophyll, carotenoids, phospholipids, metals, soaps and oxidation products. Bleaching is typically carried out under vacuum to minimize possible oxidation. Generally the goal of bleaching is to reduce the color pigments in order to produce an oil of acceptable color and to reduce the oxidation tendency of oil.

Optionally the triglyceride structures of the feedstock may be decomposed by prehydrogenating the double bonds using reduced reaction temperature with NiMo or other catalyst, prior to the of by hydrodeoxygenations in order to prevent double bond polymerisation of unsaturated triglycerides.

The process according to the invention is particularly advantageous when the fresh feed contains more than 5% of free fatty acids and even more than 10% of free fatty acids. Thus also naturally occurring fats and oils containing significant amounts of free fatty acids can be processed without the removal of free fatty acids.

In the following the process according to the invention comprising a hydrotreating step and an isomerisation step is described in more detail.

Hydrotreating of Bio Oils and Fats

In the first step of the process, i.e. in the hydrotreating step, fatty acids, triglycerides and other fatty acid derivatives comprised in the feed are deoxygenated, denitrogenated and desulphurised.

The feed comprises fresh feed and at least one dilution agent and the ratio of the dilution agent/fresh feed is 5-30:1, preferably 10-30:1, most preferably 12-25:1.

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The dilution agent is selected from hydrocarbons and recycled product of the process i.e. product recycle or mixtures thereof.

In the hydrotreating step, the pressure range may be varied between 20 and 150 bar, preferably between 50 and 100 bar, and the temperature between 200 and 400° C., preferably between 250 and 350° C. and most preferably between 280 and 340° C.

It was found that the selectivity of decarb-reactions and the deoxygenation through decarb-reactions can be promoted during hydrotreating over the hydrotreatment catalyst, by using sulphur content of 50-20000 w-ppm, preferably 1000-8000 w-ppm, most preferably 2000-5000 w-ppm of sulphur in the total feed, calculated as elemental sulphur. The specific sulphur content in the feed is able to double the extent of n-paraffins formed by removal of COx. Complete deoxygenation of triglycerides by decarb-reactions can theoretically lower the consumption of hydrogen about 60% (max) compared with pure deoxygenation by hydrogen.

At least one organic or inorganic sulphur compound may optionally be fed along with hydrogen or with the feed to achieve the desired sulphur content. The inorganic sulphur compound can be for example H₂S or elemental sulphur or the sulphur compound may be an easily decomposable organic sulphur compound such as dimethyl disulphide, carbon disulfide and butyl thiol or a mixture of easily decomposable organic sulphur compounds. It is also possible to use refinery gas or liquid streams containing decomposable sulphur compounds.

In the hydrotreatment/hydrodeoxygenation step, known hydrogenation catalysts containing metals from Group VIII and/or VIB of the Periodic System may be used. Preferably, the hydrogenation catalysts are supported Pd, Pt, Ni, NiMo or a CoMo catalyst, the support being alumina and/or silica, as described for instance in FI 100248. Typically, NiMo/Al₂O₃ and CoMo/Al₂O₃ catalysts are used.

In order to control the increase of temperature resulting from the aforementioned reactions over catalyst beds and side reaction formation, an improved reactor configuration is presented in FIG. 1. The hydrotreatment section comprises one or more catalyst beds in series, dilution agent introduction on the top of the first catalyst bed and fresh feed, recycle liquid and hydrogen introduction on top of each catalyst beds. If the dilution agent is product recycle, the product recycle/fresh oil-ratio is from 5-30:1, preferably 10-30:1 and most preferably 12-25:1. The catalyst beds can be located in same pressure vessel or each bed in a separate pressure vessel. Hydrogen is fed in excess to the theoretical chemical hydrogen consumption and the feedstock is converted totally or almost totally within each catalyst bed. Using these procedures, harmful, partially converted product intermediates are avoided, the temperature needed for reaction initiation is achieved in the beginning of each catalyst bed, the rise of reaction heating is controlled in the catalyst beds and the catalyst life is improved considerably.

Hydrodeoxygenation of triglycerides facilitates controlled decomposition of the triglyceride molecule contrary to uncontrolled cracking. Double bonds are also hydrogenated during the controlled hydrotreatment. Light hydrocarbons and gases formed, mainly propane, water, CO₂, CO, H₂S and NH₃ are removed from the hydrotreated product.

It was surprisingly observed in examples that product recycle dilution can prevent or remarkably decrease the reactions between free fatty acids and the formation of high molecular weight compounds during hydrotreating, when at least 5:1 (product recycle):(fresh oil)-ratio was used. The effect of product recycle is based on two phenomena: dilution

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effect of recycle and more controllable and reduced reaction temperatures used over catalyst bed during hydrodeoxygenation. Higher temperatures and especially hot spots of catalyst bed promote ketonisation reactions. Due to this invention, it is possible to use various sources of bio oils and fats without the need to remove fatty acids. After the hydrotreatment step, the product is subjected to an isomerization step. Isomerisation of N-Paraffins Formed During Hydrotreatment

In the second step of the process, i.e. in the isomerization step, isomerization is carried out which causes branching of the hydrocarbon chain and results in improved performance of the product oil at low temperatures. The isomerisation produces predominantly methyl branches. The severity of isomerisation conditions and choice of catalyst controls the amount of methyl branches formed and their distance from each other and therefore cold properties of bio diesel fraction produced. The product obtained from the hydrotreatment step is isomerised under isomerisation conditions with an isomerisation catalyst.

In the process according to the invention, the feed into the isomerisation reactor is a mixture of pure n-paraffins and the composition of it can be predicted from the fatty acid distribution of individual bio oils. During the hydrotreating step of the process, triglyceride oils and other fatty acid derivatives and fatty acids are almost theoretically converted to n-paraffins. Additionally propane is formed from the glycerol part of triglycerides, water and COx from carboxylic oxygen, H₂S from organic sulphur compounds and NH₃ from organic nitrogen compounds. It is substantial for the process that these gas phase impurities are removed as completely as possible before the hydrocarbons are contacted with the isomerization catalyst.

The isomerization step may comprise an optional stripping step, wherein the reaction product from the hydrotreatment step may be purified by stripping with water vapour or a suitable gas such as light hydrocarbon, nitrogen or hydrogen. The optional stripping step is carried out in counter-current manner in a unit upstream of the isomerization catalyst, wherein the gas and liquid are contacted with each other, or before the actual isomerization reactor in a separate stripping unit utilizing the counter-current principle.

In the isomerisation step, the pressure varies in the range of 20-150 bar, preferably in the range of 30-100 bar and the temperature varies between 200 and 500° C., preferably between 280 and 400° C.

In the isomerisation step, isomerisation catalysts known in the art may be used. Suitable isomerisation catalysts contain a molecular sieve and/or a metal selected from Group VIII of the Periodic Table and/or a carrier. Preferably, the isomerisation catalyst contains SAPO-11 or SAPO-41 or ZSM-22 or ZSM-23 or ferrierite and Pt, Pd or Ni and Al₂O₃ or SiO₂. Typical isomerization catalysts are, for example, Pt/SAPO-11/Al₂O₃, Pt/ZSM-22/Al₂O₃, Pt/ZSM-23/Al₂O₃ and Pt/SAPO-11/SiO₂. Most of these catalysts require the presence of hydrogen to reduce the catalyst deactivation.

An isomerised product, which is a mixture of branched hydrocarbons and preferably branched paraffins boiling in the range of 180-350° C., the diesel fuel range, and having one carbon atom less than the original fatty acid chain, is obtained. Additionally some gasoline and gas may be obtained.

ADVANTAGES OF THE INVENTION

The invention provides a method for reducing the formation of higher molecular weight compounds during the

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hydrotreatment of a feed obtained from plant oils and animal fats and which may contain free fatty acids.

It was surprisingly found that the problems of prior art processes may be avoided or at least significantly reduced by the improved process according to the invention, comprising a hydrotreatment step and an isomerisation step wherein product recycle or another dilution agent in the hydrotreatment step in combination with reduced operation temperature result in important improvements, particularly when the fresh feed contains more than 5 wt % of free fatty acids. A special reactor configuration and high dilution of fresh feed introduced into hydrotreatment are used in the method. The extent of side reactions is decreased and the stability of catalyst during hydrotreating is increased during the hydrotreatment step.

In the examples it was seen that the ratio of at least 5:1 (recycle:fresh) significantly decreased the formation of high molecular weight products, when the feedstock contains 10 wt-% of free fatty acids (calculated from fresh oil) is used. Using at least 5:1 recycle ratio and reduced reaction temperature, free fatty acids can be processed without the need for deacidification. High quality hydrocarbons are obtained, suitable for the diesel fuel pool with high yield.

The invention is illustrated in the following with examples presenting some preferable embodiments of the invention. However, it is evident to a man skilled in the art that the scope of the invention is not meant to be limited to these examples.

EXAMPLES

All hydrotreatment tests were performed in the presence of hydrogen.

Example 1

Comparative Example

Tall Oil Feed (100% Free Fatty Acids) without Product Recycle

Hydrotreating of tall oil (100% free fatty acids) with NiMo catalyst was carried out at 50 bars pressure, LHSV 1.5 and reaction temperatures from 340-360° C. without product recycle. Hydrogen oil ratio was 900 normal liters H₂ per liter oil fed. The hydrotreating of tall oil 100% free fatty acid feed caused rapid deactivation of NiMo catalyst, and formation of heavy weight compounds and aromatics was observed. Bromine indexes increased during the run even if temperature compensation of catalyst was used (FIG. 8). Product oil contained about 7 wt-% aromatics and about 7 wt-% heavies (>375° C. boiling). Density (50° C.) of product oil was high 777.1 kg/m³ compared to typical values with rapeseed oil hydrotreated product oil (761-762 kg/m³) using lower reaction temperature and optimized reaction conditions.

Example 2

Comparative Example

Tall Oil Fatty Acid Feed (100% FFA) at High Reaction Temperatures Without Product Recycle

Hydrotreating of tall oil fatty acid feed (100% FFA) at high reaction temperatures 370-385° C. was carried out without product recycle. Rapid deactivation of NiMo catalyst and formation of heavy weight compounds and aromatics was observed. Density of hydrotreated oil (table 1) was significantly

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higher than in rapeseed oil runs (typically 761-762 kg/m³). Both oils contained mainly C18 fatty acids (~90-wt-%) and rather steady formation of water was observed during run. During the tall oil hydrotreating about 7-8 wt-% heavier molecular weight compounds and 8.1 wt-% aromatics were formed. These side reactions are caused by concentrated fatty acid feed and too high reaction temperatures. Deactivation of catalyst is clearly seen from increasing bromine indexes. During the satisfactory operation bromine index should be below 50. Table 1 describes densities, bromine indexes, reaction temperatures and water formed during test runs for 2 to 14 days using tall oil fatty acid feed (100% FFA) without recycling.

TABLE 1

Duration of test run	2nd day	4th day	6th day	9th day	11th day	12th day	13th day	14th day
Temperature, ° C.	370	375	378	381	385	385	385	385
Density, 50° C., kg/m ³	771.8	773.1	773.7	776.5	779.1	779.8	780.5	781.2
Bromine index	101	150	188	198	247	269	300	330
Product water, %	9.37	9.5	9.81	10.3	10.2	10.0	10.1	10.2

Example 3

Comparative Example

Effect of Metal Impurities of Bio Oils on the Catalyst Performance

Tube reactor hydrotreatment test runs were carried out using crude rapeseed oil, crude animal fat and purified rapeseed oil. Analysis of these feeds are shown in Table 2. Crude feeds contained significant amount of metals, organic phosphorus, sulphur and nitrogen compounds. Purified feeds contained only trace levels of these impurities

TABLE 2

Impurity levels of crude and purified plant oils and animal fats				
Impurity	Unit	Crude Rapeseed oil	Purified Rapeseed oil	Crude Animal fat
Metals (total)	ppm	90	~0	162
Org. nitrogen	ppm	33	7.2	1125
Free Fatty acid, GPC	Wt-%	0.8	0.7	10.8
Total Acid Number	mg KOH/g	1.0	0.1	21.5
Phosphorous	ppm	110	<1	86
Sulphur (original)	ppm	3	1	85

Test runs using crude, unpurified oils/fats showed that catalyst needed higher temperatures to work properly, but gradually lost its activity (FIG. 5). Triglycerides and increased bromine number of product oil was found. High amount of metals were also detected on to the catalyst. Temperature profile of the catalyst bed showed that top of the catalyst bed was deactivated and reaction section moved forward (FIG. 4), when reactor heating was maintained steady. Metals adsorbed on to the catalyst also promote side reactions like decarb-reactions.

First hydrotreatment test run was carried out using crude rapeseed oil. Purified rapeseed oil was used as a reference feed. Purified rapeseed oil achieved complete HDO conver-

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sion at 305° C. using WHSV=2. Crude rapeseed oil gave total HDO conversion not until reaction temperature 330° C. was used with space velocity WHSV=1. It was however seen from temperature profiles over the catalyst bed that first part of catalyst was deactivated very quickly. In FIG. 4, reaction temperature profile over catalyst bed and performance of crude rapeseed oil are presented.

Second hydrotreatment test run was carried out using purified rapeseed oil and crude animal fat. Purified rapeseed oil was used as a reference feed. Purified rapeseed oil with product recycle achieved complete HDO conversion at 305° C. using WHSV=1. Crude animal fat with product recycle did not give complete HDO conversion at 305° C. using WHSV=1. It was seen from GPC analyses that product oil contained triglycerides and catalyst also significantly deactivated during crude animal fat feed. Pumping problems was also observed during crude animal fat feeding. Performance of crude animal fat is presented in FIG. 5.

Example 4

Comparative Example

Effect of Free Fatty Acids (10 Wt-% in Fresh Feed)
on the Formation of High Molecular Weight
Hydrocarbons

Hydrotreatment was carried out using purified rapeseed oil as reference feed without product recycle. A test run was carried out at 305° C. and 50 bars pressure using WHSV=1 and H₂/oil-ratio=1000. Sulphur content of feed was 570 ppm. During a second hydrotreatment test period stearic acid was fed (10 wt-% from rapeseed oil) along with purified rapeseed oil using same reaction conditions without product recycle. It was right away observed that the extent of high molecular weight compounds increased gradually from initial level ~3 wt-% to ~8 wt-%. These higher molecular weight compounds

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(molecular weight double or more of the feed) are not in the boiling range of diesel fuel and thus decrease diesel yield and potentially shorten the catalyst life. Thus free fatty acids in bio oils make their processing more difficult. In FIG. 2 the increase of formation of high molecular weight hydrocarbons is observed, when 10 wt-% free fatty acids was fed along with purified rapeseed oil triglycerides without product recycle.

Example 5

Effect of Product Recycle on Preventing Formation
of Unwanted Heavy Side Reaction Compounds
when the Feed Contained 10 wt-% Free Fatty Acids

A hydrotreatment test run was carried out using 10 wt-% stearic acid containing purified rapeseed oil as reference feed without product recycle under following reaction conditions: WHSV=1, 50 bars, 305° C., H₂/oil-ratio=1000 and sulphur content of feed=570 ppm. During the second hydrotreatment test run period same feed was diluted with product hydrocarbons so that (fresh oil)/(product recycle)-ratio was 1:5. WHSV of fresh oil was maintained at 1, therefore WHSV of total oil feed increased to 6. The reaction temperature was kept at 305° C. and reaction pressure at 50 bars. H₂/(fresh oil)-ratio was maintained at 1000. HDO product (n-paraffins) simulated product recycle, which was mixed in advance with fresh oil. The initial content of heavy hydrocarbons in the recycle was ~0.4 wt-%.

It was unexpectedly observed that the formation of heavy hydrocarbons was almost totally prevented or at least very significantly decreased when product recycle was used (FIG. 3). This is most probably caused by significantly diminished side reactions of free fatty acids wherein a carboxylic acid molecule can react with another carboxylic acid molecule to form a higher molecular weight compounds. In FIG. 3 the effect of product recycle on preventing the formation of unwanted higher molecular weight by-product is presented. Table 3 presents analysis results of the feed and products.

TABLE 3

Analysis results of the feed and products									
Property	Method	Units	Feed analyses				Product analyses		
			AR	Recycle feed	AR (10% SA) + REC	AR (10% SA) + 1:5	AR + 10 wt-% stearic acid without recycle	AR + 10 wt-% SA + Recycle after 196 hours	AR + 10 wt-% SA + Recycle after 552 hours
Density, 15° C. calc.	D 4052	kg/m ³	920.4	788.1	915.8	807.2	790.8	788.3	788.3
Density, 50° C.	D 4053	kg/m ³	897.6	761.4	893.2	781.2	764.2	761.7	761.7
Br-index	D 2710	mg/100 g		53.7			21.5		26
Br number	D 1159	g/100 gr	56		49.1	6.3			
Iodinenumber	D 5554	g/100 g	112		103	18			
HC	GPC	area-%		99.6		83.0	94.3	99.6	99.6
Fatty acids	GPC	area-%	0.7	0	10.6	1.8	0	0	0
Heavy HC	GPC	area-%	0	0.4		0.5	5.7	0.4	0.4
Diglycerides	GPC	area-%	2.3	0	2.4		0	0	0
Triglycerides	GPC	area-%	97	0	87	14.7	0	0	0

SA = Stearic acid,
AR = purified rapeseed oil,
REC = product recycle,
HC = hydrocarbons, heavy
HC = high molecular weight hydrocarbons

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Example 6

Comparative Example

The Effect of Lower Reaction Temperature on the Selectivity of N-Paraffins and Oil Yield

Studies were carried out with NiMo catalyst using rapeseed oil as feed and reaction temperatures 280-330° C. and

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main component of feed, but it was modified with animal fat, fractions of free fatty acids, crude rapeseed oil, and lecithin in order to get suitable specification of impurities of test feed. Fresh feed analysis is presented below in table 4. Fresh oil was then diluted in advance with 1:5 ratio of HDO product (simulates product recycle). The duration of test run was over 9 months. Stable operation was maintained (table 4 and FIG. 7) and the formation of heavies was steady over the whole test run FIG. 7.

TABLE 4

			Stability of catalyst				
			Product oil analysis				
Run duration			Fresh	1898	3408	5601	
Analysis	Method	Unit	Feed analysis	383 hours	hours	hours	hours
Density, 15° C.	D 4052	kg/m ³	804.9	787.4	785.6	785.3	784.9
Density, 50° C.	D 4052	kg/m ³	778.8	760.7	758.9	758.6	758.1
Br-index	D 2710	mg/100 g	29200	33	48	33	11
HC	GPC	area-%	0	99.3	99.4	99.3	99.4
Fatty acids	GPC	area-%	1.2	0	0	0	0
Monoglyc/high molec. weight HC	GPC	area-%	0.3	0.7	0.6	0.7	0.6
Diglycerides	GPC	area-%	6.3	0	0	0	0
Triglycerides	GPC	area-%	92.1	0	0	0	0
TAN	D664	mg KOH/g	2.1	~0	~0	~0	~0
Sulphur	D 5453	ppm	3	1.2	2.0	2.7	2
Nitrogen	D4629	mg/kg	6	<1	<1	1.2	<1
Sodium, oil	AAS	mg/kg	3	0.4	<0.1	<0.1	<0.1
Calcium, oil	AAS	mg/kg	2	0.3	<0.1	<0.1	<0.1
Magnesium, oil	AAS	mg/kg	0.3	<0.1	<0.1	<0.1	<0.1
Molybdenum, oil	AAS	mg/kg	—	<0.5	<0.5	<0.5	<0.5
Aluminum, oil	ICP metals	mg/kg	<2	<2	<2	<2	<2
Iron, oil	ICP metals	mg/kg	<1	<1	<1	<1	<1
Nickel, oil	ICP metals	mg/kg	<1	<1	<1	<1	<1
Phosphorus, oil	ICP metals	mg/kg	4	<1	<1	<1	<1

340-360° C., WHSV=1 and reactor pressure of 50 bars. Alkali raffinated rapeseed oil triglycerides contained mainly C₁₈ fatty acids. C₁₈ fatty acids contributed about 89 wt-% of all fatty acids in rapeseed oil. Theoretical amount of n-paraffins formed from rapeseed oil fed is about 86.4 wt-% (calculated from rapeseed oil fed).

Complete HDO conversion with almost theoretical n-paraffin yield was accomplished, when well controlled reaction temperatures <330° C. were used. Almost theoretical n-paraffin yields tell us from complete HDO conversion and very controllable operation without significant side reactions. High amount of side reactions (cyclisation, aromatisation and cracking) and low n-paraffin yield were observed when unnecessary high reaction temperatures 340-360° C. was used. In FIG. 6 the conversion of rapeseed oil triglycerides to n-paraffins is presented.

Example 7

Stability of Catalyst

The stability of NiMo-catalyst using palm oil model feed (impurities added) along with product recycle (catalyst life test) was carried out using following reaction conditions: Reaction temperature=300-305° C., Reactor pressure=40 bars, WHSV (fresh)=0.5, WHSV (total)=3, H₂/Oil (fresh)=900, Sulphur in feed=100 w-ppm. Palm oil was used as a

The invention claimed is:

1. A process for the manufacture of diesel range hydrocarbons comprising:

combining a fresh feed stream of biological origin and a stream of diluting agent containing hydrocarbons to form a total feed stream,

introducing the total feed stream to a hydrodeoxygenation step,

hydrodeoxygenating the total feed, in the hydrodeoxygenating step,

introducing the hydrodeoxygenated product to an isomerization step, and

isomerizing the hydrodeoxygenated product in the isomerization step,

wherein

the total feed stream contains less than 10 w-ppm alkali and alkaline earth metals, calculated as elemental alkali and alkaline earth metals, less than 10 w-ppm other metals, calculated as elemental metals, and less than 30 w-ppm phosphorous, calculated as elemental phosphorous.

2. The process according to claim 1, wherein the total feed stream contains less than 5 w-ppm alkali and alkaline earth metals, calculated as elemental alkali and alkaline earth metals, less than 5 w-ppm other metals, calculated as elemental metals, and less than 15 w-ppm phosphorous, calculated as elemental phosphorous.

3. The process according to claim 1, wherein the total feed stream contains less than 1 w-ppm alkali and alkaline earth metals, calculated as elemental alkali and alkaline earth metals, less than 1 w-ppm other metals, calculated as elemental metals, and less than 5 w-ppm phosphorous, calculated as elemental phosphorous.

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4. The process according to claim 1, wherein the fresh feed stream contains more than 5 wt-% of free fatty acids.

5. The process according to claim 1, wherein the ratio diluting agent/fresh feed in the total feed is 5-30:1.

6. The process according to claim 1, wherein the ratio diluting agent/fresh feed in the total feed is 10-30:1.

7. The process according to claim 1, wherein the diluting agent containing hydrocarbons is selected from the group of hydrocarbon of biological origin, hydrocarbon of non-biological origin and a recycled product from the process.

8. The process according to claim 1, wherein the total feed stream contains 50-20000 w-ppm of sulphur, calculated as elemental sulphur.

9. The process according to claim 1, wherein the fresh feed of biological origin is selected from plant oils/fats, animal fats/oils, fish fats/oils, fats contained in plants bred by means of gene manipulation, recycled fats of the food industry and mixtures thereof.

10. The process according to claim 1, wherein the fresh feed stream is selected from rapeseed oil, colza oil, canola oil, tall oil, sunflower oil, soybean oil, hempseed oil, olive oil, linseed oil, mustard oil, palm oil, peanut oil, castor oil, coconut oil, lard, tallow, train oil or fats contained in milk.

11. The process according to claim 1, wherein the fresh feed stream comprises a mixture of a feed of biological origin and at least one hydrocarbon.

12. The process according to claim 1, wherein the hydrodeoxygenating step takes place on a hydrodeoxygenating catalyst bed system comprising one or more catalyst beds.

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13. The process according to claim 1, wherein the pressure during the hydrodeoxygenating step is in the range of 2-15 MPa.

14. The process according to claim 1, wherein the pressure during the isomerisation step is in the range of 2-15 MPa, and the temperature is between 200 and 500° C.

15. The process according to claim 1, wherein the hydrodeoxygenating is carried out in the presence of a hydrogenation catalyst, said hydrogenation catalyst containing a metal from the Group VIII or VIB of the Periodic System.

16. The process according to claim 1, wherein the hydrodeoxygenating catalyst is a supported Pd, Pt, Ni, NiMo or a CoMo catalyst, the support being alumina and/or silica.

17. The process according to claim 1, wherein an isomerization catalyst containing molecular sieve is used in the isomerization step.

18. The process according to claim 17, wherein the isomerization catalyst contains a metal from the Element Group VIII.

19. The process according to claim 17, wherein the isomerization catalyst contains Al_2O_3 or SiO_2 .

20. The process according to claim 17, wherein the isomerization catalyst contains SAPO-11 or SAPO-41 or ZSM-22 or ZSM-23 or ferrite and Pt or Pd or Ni and Al_2O_3 or SiO_2 .

* * * * *

CERTIFICATE OF SERVICE

I certify that I electronically filed the foregoing BRIEF FOR APPELLANT-PATENT OWNER NESTE OIL OYJ using the Court's CM/ECF filing system. Counsel registered with the CM/ECF system have been served by operation of the Court's CM/ECF system per Fed. R. App. P. 25 and Fed. Cir. R. 25(a) on this 21st day of January, 2015:

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CERTIFICATE OF COMPLIANCE

The undersigned certifies that this brief complies with the type-volume limitations of Fed. R. App. P. 32(a)(7)(B). This brief is printed in 14-point Times New Roman font and contains 11,767 words.

January 21, 2015

/s/ Michael J. Flibbert